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THE Journal OF THE AMERICAN LEATHER CHEMISTS ASSOCIATION

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of the

AMERICAN LEATHER CHEMISTS ASSOCIATION

Vol. LIII JANUARY 1958 No. 1

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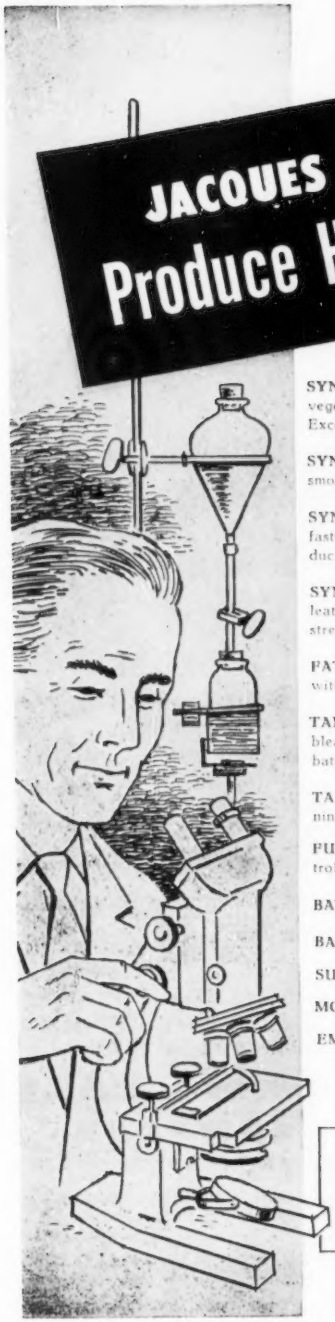

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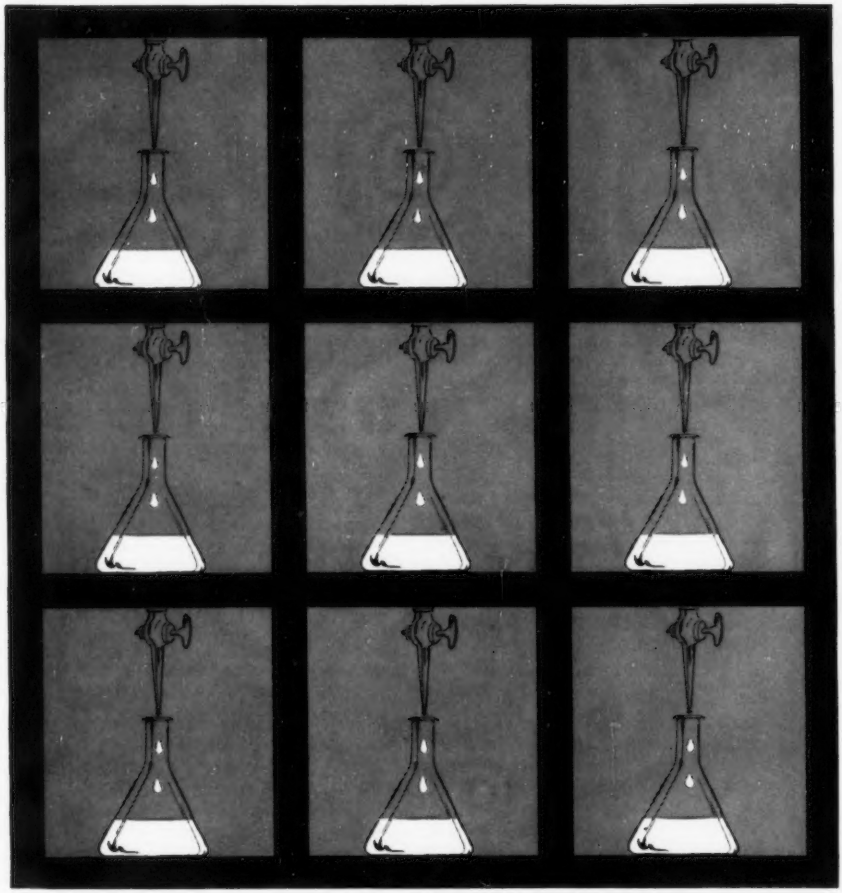

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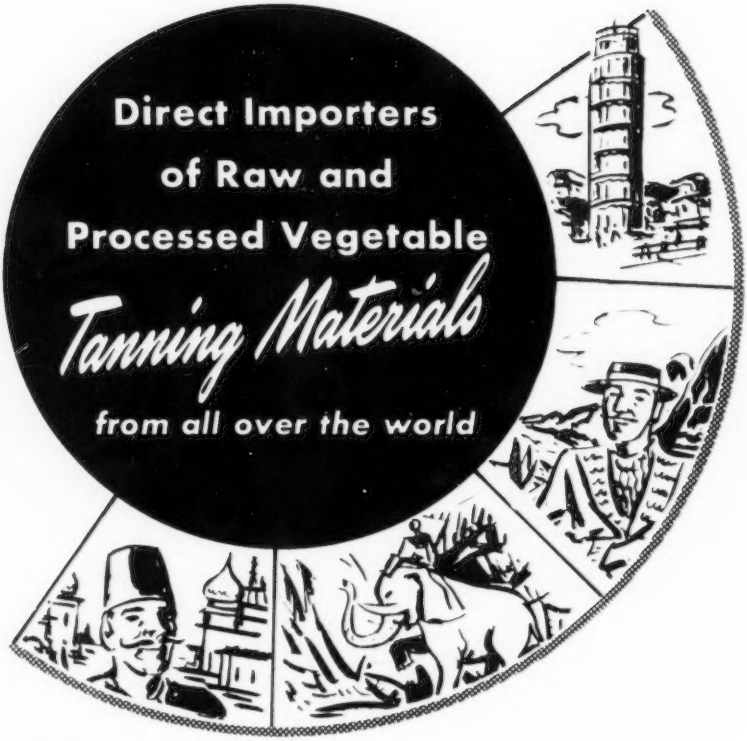

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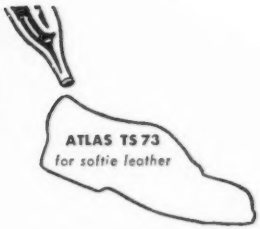

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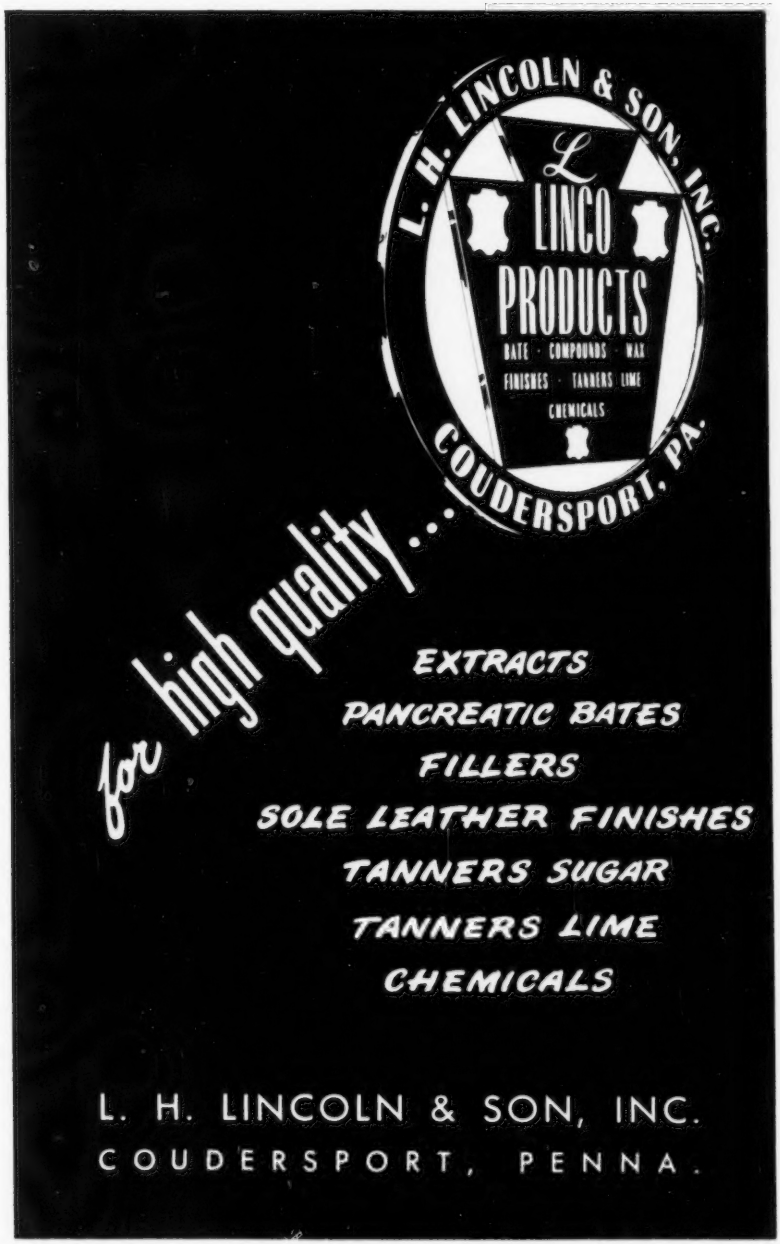
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HYDROXYPROLINE ANALYSIS AS A TOOL FOR TANNERY CHEMISTS*

ROBERT M. LOLLAR

Tanners' Council Research Laboratory
University of Cincinnati
Cincinnati 21, Ohio

ABSTRACT

Data have been presented on the precision of the determination of hydroxyproline by a modified form of the[1] Neuman-Logan colorimetric procedure. The practical application of the method to the determination of "leather-making substance" in samples taken from skins and hides at process stages from flaying through curing and the tannery beamhouse processes is illustrated by an example. Suggestions are presented for studies designed to improve the method further, in the hope that its adoption by industry as a common control method will be hastened.

—x—x—

INTRODUCTION

Leather chemists need a specific method for the determination of the amount of collagen (white connective tissue protein) in skins and hides, beamhouse liquors, and leather. Customary analyses for total Kjeldahl nitrogen lack specificity because such hide components as hair and globular proteins and such leather components as dyes, finishes, and aminoplast resins contribute significant quantities of noncollagenous nitrogen. Therefore, estimation of the "hide substance" in the customary fashion (multiplication of the total Kjeldahl nitrogen content by the factor 5.62) cannot accurately determine the amount of collagen, or true "leather-making substance", in skins and hides or leather.

Jacobs (7) and Stubbings (12) have suggested methods for the fractional analyses of the several component proteins of animal skins and hides. However, these methods for the determination of leather-making substance, or collagenous content of skins and hides, are laborious, and the collagen content is secured indirectly by the use of the nonspecific Kjeldahl analysis of presumably pure fractions of the skin and hide components. A direct specific method would be preferable, particularly since the precision of a determination

*Presented at the Fifty-third Annual Meeting, Lake Placid Club, N. Y., June 3, 1957.

of leather-making substance must be very high before the results can have practical value.

Neuman and Logan (10) have proposed that the estimation of the hydroxyproline content of protein hydrolyzates would furnish an estimate of the collagen content of the tissue from which the hydrolyzate was prepared. Hydroxyproline is an unique imino acid found in significant quantity only in connective tissue. Collagen is quite rich in this imino acid, with mammalian collagens containing 13–14% of the acid. Globular proteins and keratinous proteins do not contain this imino acid in significant amounts. Neuman and Logan (10) found that "elastin", prepared by boiling *Ligamentum nuchae* with water for 24 hours, contains 1.8% hydroxyproline. However, the amount of yellow elastic tissue in skins and hides is small, so that this source of hydroxyproline does not contribute a significant error to the determination of leather-making substance based upon hydroxyproline analyses. Further the analytical procedure of Neuman and Logan is quite specific for hydroxyproline, even though tyrosine and tryptophan cause some interference. However, the amount of these amino acids in hide hydrolyzates is small, so that error arising from this source should also be small. The hydroxyproline method therefore seemed to us to be worthy of examination to evaluate its potential use in the determination of leather-making substance.

O'Flaherty (11) has suggested that tanners should be concerned with the amount of leather-making substance in lots of skins and hides which they purchase, in addition to considering the invoice weight of the lot; this would of course require such analyses to have high precision. This suggestion has recently been given additional significance by the observation of Hauck and Lollar (5) that the strength characteristics of chrome-tanned elk-type side leather are dependent to a significant extent on the amount of leather-making substance contained in the four commercial hide lots and in the leather made from these hides. This observation indicates the need for further consideration of O'Flaherty's suggestion, so that study of the precision of the hydroxyproline analysis is indicated.

Tannery chemists often wish to know whether the beamhouse operations are solubilizing any collagenous protein from the skins and hides being processed. Specificity in the analytical procedure is quite important for this purpose, since one function of the beamhouse operation is the removal of noncollagenous proteins from the skins and hides. Application of the nonspecific Kjeldahl nitrogen determination to these process liquors cannot differentiate the nitrogen which originates from the collagenous fibrous protein from that which originates from the soluble proteins of the skin or hide; hence the tannery chemist has been forced to depend upon fractional precipitation methods of doubtful validity on such process liquors whenever he wished to consider this question. The hydroxyproline analysis of the waste liquors would not suffer this defect, since the presence of this imino

acid in the beamhouse waste liquors would definitely indicate some solubilization of collagenous fibrous tissue.

Recent increasing use of various aminoplast resinous materials in leather manufacture has introduced a complication into the analysis of leather, since the customary Kjeldahl nitrogen data are noninterpretable due to the simultaneous determination of aminoplast- and collagenous-nitrogen. Hydroxyproline analyses would not report the aminoplast nitrogen; hence this analytical procedure could be valuable in the analysis of leather. This would require the development of a hydrolysis procedure capable of separating the free imino acid from the leather complex without the destruction of the hydroxyproline. This analysis will require further study, but it does seem to be a possibility after the basic hydroxyproline procedure has been developed for use in the leather industry.

This paper will present information which we have secured in our use of the hydroxyproline analysis over the past several years. In particular, our efforts to improve the precision of the technique will be discussed, with some preliminary information on the results secured when the method has been applied to skins and hides. It is hoped that publication at this time will stimulate others to employ the method and thus that the day when it will become a practical tool in the leather industry will be hastened.

EXPERIMENTAL METHODS AND REAGENTS

Our early use of the Neuman and Logan (10) procedure for the determination of hydroxyproline disclosed that the precision was too low for use in the practical determination of leather-making substance. Howard (6) and Eling and Lollar (3) encountered rather large day-wise variability in their standard curves. Further, Eling and Lollar were at times unable to secure consistent results with the method. After further consultation with Dr. Logan's research group, which was continuing to use the method, and after additional study of the method in this laboratory, it now seems possible to describe a specific set of applicable conditions for use of hydroxyproline analyses on specimens of cured skins and hides.

The hydrolysis of the skin and hide tissue was the first procedure studied. Howard (6) had previously considered the effect of acid strength, the ratio of acid volume to the weight of dehydrated steerhide corium, and the time of hydrolysis under reflux conditions. Formol titrations and ammonia nitrogen analyses were employed to follow the rate of hydrolysis and to determine when hydrolysis was complete. Based upon this study, he selected a 16-hour reflux hydrolysis with 6 *N* HCl, using a 6 to 1 float ratio.

Howard's technique has been employed as our basic hydrolysis procedure. Comparison of the use of 6 *N* HCl and of 6 *N* H_2SO_4 disclosed no significant difference for either acid. The latter acid has been used in place of the former, since the use of sulfuric acid permits the determination of total

Kjeldahl nitrogen in a separate aliquot of the hydrolyzate. The specific hydrolysis procedure employed in our analyses of cured skin and hide specimens includes:

(*a*) Weigh 5 to 6 g. of the diced hide specimen into a 250- or 300-ml. Soxhlet flask with a standard taper adapter top.

(*b*) Add 30 ml. of 6 *N* H_2SO_4.

(*c*) Hydrolyze under a reflux condenser for 16 hr.

(*d*) The hydrolyzate is extracted with chloroform to remove native skin lipides. The hydrolyzate is transferred quantitatively to a 500-ml. separatory funnel, diluting it with 150 ml. of distilled water during the transfer. The hydrolyzate is then extracted with three separate 90-ml. portions of chloroform, combining the extracts in a weighed tannin dish by evaporation of the chloroform, employing a steam bath, followed by determination of the dry weight (100°C.) of the residue. This weight is calculated as the percent of chloroform-extractable material, or fat, in the hide specimen. (It has been found that a "butter" of glycerine and bentonite serves as an effective lubricant for the separatory funnel stopcocks.)

(*e*) The lipide-free hydrolyzate is quantitatively transferred to a 250-ml. volumetric flask and diluted to volume with distilled water. One portion, of 50 to 100 ml., is removed for the determination of the total Kjeldahl nitrogen in the hide hydrolyzate; this nitrogen content, expressed on the hide-specimen basis, is converted to the total protein in the hide specimen by the use of the factor 5.62. Another portion of the hydrolyzate is taken for the determination of the amount of hydroxyproline according to the techniques discussed in this paper.

The reagents employed in the determination of hydroxyproline must be of the highest purity. It has been our practice to use reagent-grade or American Chemical Society approved quality chemicals; sodium hydroxide, cupric sulfate, hydrogen peroxide, and sulfuric acid which we used are covered by these standards. Normally, it is possible to use n-propyl alcohol (A-414 Fisher Certified Grade, supplied by the Fisher Scientific Company, Pittsburgh 19, Pa.) without purification, but on occasion erratic results attributed to the n-propyl alcohol have been encountered.

Ehrlich's reagent, para-dimethylaminobenzaldehyde, is the critical reagent for this procedure. Neuman and Logan (10) describe a purification procedure for the reagent; this procedure has been used and found satisfactory on some lots but not on other lots of the reagent. However, it has been found that the Matheson, Coleman and Bell Division of the Matheson Co., Norwood, Ohio, provides an acceptable product for use without purification under their code number of 1606. This product is packed in an inert argon atmosphere;

our experience has indicated that 10- or 25-gram bottles stored in a refrigerator may be used without further purification until the bottle contents have been consumed.

The accuracy of the results secured from the hydroxyproline analysis will of course be directly dependent upon the purity of the hydroxyproline used for the determination of the colorimetric reference standard curve. Several specialty chemical supply firms offer 1 (—) hydroxyproline with a total nitrogen content approximately equal to the theoretical value 10.68%, with a specific rotation approximating the standard value of —75.2 (D-line of sodium, 22.5°C., in water at a concentration of 1 g. per 100 ml.) and with no alpha amino nitrogen. It has been our experience that lots of 1 (—) hydroxyproline secured from General Biochemicals, Inc., Chagrin Falls, Ohio, have yielded optical-density values as high as any of the products secured from competitive commercial sources. We have found this product to be free of moisture, ash, chlorides, and ammonia nitrogen. Its total nitrogen value is somewhat below theoretical, with a value as low as 10.3% having been found. However, since no other product has been found which yields higher optical-density values, and since no independent, absolute method is available to us to determine the absolute purity of the hydroxyproline, we have used this product as our reference standard.

The details of the colorimetric procedures employed will appear in a later section of this paper. It should be noted here that the Beckman DU spectrophotometer, using 1-cm. rectangular Corex cells, has been employed in the work reported here. However, it has also been found that the Klett-Summerson photoelectric colorimeter with a 560-mμ interference filter may be used very satisfactorily with the method. The selection of a 560-mμ filter is in accordance with the fact that the maximum optical density of the developed color is attained at this wavelength.

STUDY OF THE PRECISION OF THE COLOR SYSTEM

During our use of the Neuman-Logan procedure (10) for the determination of hydroxyproline we have found that certain variations in the procedural details have resulted in improved day-wise precision in the method. As a result of our study of this method it is recommended that the following procedure be employed:

Reagents

(*a*) Hydroxyproline-concentrated reference solution

Dissolve 25.0 mg. of 1 (—) hydroxyproline in distilled water and quantitatively dilute to 500 ml. with distilled water in a standard taper volumetric flask. This concentrated standard, containing 50 μg. of hydroxyproline per ml. can be kept for one week in a refrigerator.

The following dilute hydroxyproline standards are prepared from the above concentrated standard:

i—10 μg. per ml.—Dilute 20 ml. of the concentrated standard to 100 ml. in a standard taper volumetric flask, using distilled water.

ii—15 μg. per ml.—Dilute 30 ml. of the concentrated standard to 100 ml. as in (i).

iii—20 μg. per ml.—Dilute 40 ml. of the concentrated standard to 100 ml. as in (i).

iv—25 μg. per ml.—Dilute 50 ml. of the concentrated standard to 100 ml. as in (i). These four dilute solutions are also held under refrigeration when not being used; they are also discarded after one week of storage.

(*b*) Copper sulfate solution—0.01 *M* $CuSO_4$

Dissolve 0.79 g. $CuSO_4$ or 1.249 g. $CuSO_4 \cdot 5\ H_2O$ in distilled water and dilute to 500 ml. This solution may be used as long as it retains its clarity and freedom from contamination.

(*c*) Sodium hydroxide solution—2.5 *N* NaOH

Dissolve 50 g. of reagent grade NaOH pellets in CO_2-free distilled water, diluting to 500 ml. This solution may be used as long as it does not become cloudy or contaminated.

(*d*) 1.8% hydrogen peroxide

Dilute 6 ml. of A.C.S.-grade 30% H_2O_2 to 100 ml. with distilled water. This solution is prepared daily from refrigerated 30% H_2O_2, which content has been checked by analysis.

(*e*) 3 *N* H_2SO_4

Dilute 83 ml. of reagent-grade H_2SO_4 (sp. gr. 1.84) to 1 l. with distilled water; this solution is stable unless it is contaminated.

(*f*) 5% para-dimethylaminobenzaldehyde

Dissolve 5 g. of MCB No. 1606 para-dimethylaminobenzaldehyde in 100 ml. of reagent grade n-propanol; this solution is prepared fresh each day just before it is to be used.

Procedure

(*a*) Pipette 1 ml. of the 250-ml. dilution of the extracted hydrolyzates from the hide specimens into a 50-ml. standard taper glass stoppered volumetric flask and dilute to volume with distilled water.

(*b*) Pipette 2 ml. of each of the 4 dilute hydroxyproline standards (i to iv inclusive), 2 ml. of the above 50 ml. dilution of the hydrolyzates, as well as

2 ml. of distilled water (for the reagent blank) into separate test tubes (1.8 to 2.0 mm. in diameter and 150 mm. long).

(*c*) Pipette 1 ml. of the copper sulfate solution into each test tube, shaking each test tube upon addition of the reagent.

(*d*) Pipette 1 ml. of the sodium hydroxide solution into each test tube, shaking each test tube upon addition of the reagent.

(*e*) Pipette 1 ml. of the 1.8% H_2O_2 solution into each test tube. Complete mixing of the H_2O_2 solution with tube contents should be assured by gentle agitation of each tube immediately after each individual addition of the peroxide. Slow but continued oxidation is secured by moderate agitation of racks of the test tubes at approximately 5-minute intervals. The tubes are observed for slowing down of the evolution of bubbles; a 30-minute oxidation period seems sufficient. Tubes may however be allowed to stand for a couple of hours at this stage. The oxidation is finally completed and the excess peroxide is removed by vigorous agitation of the tube contents, securing this by rapping the individual tubes against the palm of the hand until all visible evolution of bubbles ceases.

(*f*) Pipette 4 ml. of the 3*N* H_2SO_4 into the tubes and mix tube contents thoroughly. Small stirring rods are added to each tube to promote this mixing; these rods remain in the tubes during the remainder of the procedure.

(*g*) Pipette 3 ml. of the para-dimethylaminobenzaldehyde solution into the tubes and mix thoroughly. Immediately immerse the tubes into a 70°C. water bath, immersing them until the tube contents are below the water level in the bath.

(*h*) After exactly 25 minutes in the 70°C. color development bath, remove the tubes and place them in an ice water bath for 5 minutes to stop the color development reaction.

(*i*) Dilute the cooled tube contents during transfer to a 25-ml. glass-stoppered standard taper volumetric flask, with thorough mixing of the flask contents following.

(*j*) Measure the color density at 560 mμ approximately 30 minutes after the tubes have been removed from the 70°C. color development bath.

(*k*) Compare the color density values obtained from the hydrolyzate portions and from the hydroxyproline standards, using the reagent blank to standardize the spectrophotometer. This comparison assumes a linear relationship between optical density and weight of hydroxyproline present;

a later section of this paper will indicate the justification for this assumption. A graphical method of comparison is convenient.

(*l*) Compute the % hydroxyproline in the skin and hide specimen from the following formula:

$$\%\ \text{Hydroxyproline (Hide-weight basis)} = \frac{\mu\text{g. HP per 25 ml. color} \times 50 \times 250 \times 100}{1000 \times 1000 \times \text{sample weight in grams}}$$

Several details in this procedure depart from the original details of the method of Neuman and Logan (10). The developed colors have been diluted to 25 ml. to eliminate error due to variable evaporation in the color-development procedure. This greater dilution required the use of larger amounts of the hydroxyproline in the color-development solutions to give equivalent color density values; 2-ml. portions of the standards and hydrolyzates were therefore used instead of 1-ml. portions. The oxidation procedure was changed sequentially during our use of the procedure in our efforts to improve the precision of the method. First, the method was simplified by using a single 70°C. constant-temperature bath for both the removal of the excess hydrogen peroxide and for the development of the color. Later, it was found that more precise results could be secured by a lower initial concentration of hydrogen peroxide and by removal at room temperature of the excess peroxide. The peroxide concentration given above (1.8% H_2O_2) is 6% by volume of the common 30% hydrogen peroxide instead of the original concentration of 6% by weight of H_2O_2. Our experience indicated that the agitation was the significant factor in the removal of excess peroxide, and hence it has been found that it is easier to do this at room temperature.

The hydroxyproline analytical procedure in its different stages of modification was used repetitively over many months; data were thus secured which could be analyzed statistically to test the customary assumption that Beer's law is applicable and to estimate the inherent precision of the analytical method. The statistical technique of analysis of regression was employed; this technique is discussed in many standard statistical texts, and the article by Day, Del Priore and Sax (2) has been particularly useful. Table I and Figure 1 present data secured from this statistical stury of three variations in the colorimetric procedure for hydroxyproline.

Hydroxyproline standards were included whenever the hydroxyproline content of skin and hide specimens was being determined, and the optical-density values secured from these standards have been subjected to the statistical analysis. Data in Table I designated as "original procedure", shown in Figure 1 as curve *A*, were secured while we were following the details of the original Neuman and Logan procedure as precisely as possible. Data designated "intermediate procedure", which are shown by curve *B* of Figure 1, were secured with 6% H_2O_2 being used for the oxidation stage,

TABLE I

STATISTICAL ANALYSES OF THE OPTICAL-DENSITY VALUES FOR THE HYDROXYPROLINE SYSTEM

Original Procedure (10 ml)			Intermediate Procedure (25 ml.)			Procedure This Paper (25 ml.)		
Hydroxyproline	Optical Density		Hydroxyproline	Optical Density		Hydroxyproline	Optical Density	
μg/ml	Av.	Regression	μg/ml.	Av.	Regression	μg/ml.	Av.	Regression
0.38	0.057	0.064	0.4	0.076	0.082	...	.....	.....
0.45	0.085	0.077	0.8	0.139	0.135	0.8	0.172	0.175
0.75	0.126	0.134	1.0	0.165	0.162	...	.....	.....
1.13	0.211	0.205	1.2	0.192	0.189	1.2	0.247	0.244
1.5	0.273	0.275	1.4	0.225	0.216	...	.....	.....
.....	.....	.....	1.6	0.243	0.242	1.6	0.316	0.313
(2.0)	.....	(0.369)	2.0	0.290	0.296	2.0	0.379	0.382

Analyses of Regression Curve A—Figure 1				Analyses of Regression Curve B—Figure 1				Analyses of Regression Curve C—Figure 1			
Source of Variance	D.F.	Mean Square	F-Value	Source of Variance	D.F.	Mean Square	F-Value	Source of Variance	D.F.	Mean Square	F-Value
Regression	1	679,102	1525*	Regression	1	509,662	4828*	Regression	1	427,800	16,510*
Deviation	3	1078	2.42	Deviation	5	477.8	4.52†	Deviation	2	362	13.97†
Within levels	88	445.3	...	Within levels	89	105.6	...	Within levels	68	25.91	...

*Significant at 0.001 level.
†Significant at 0.01 level.

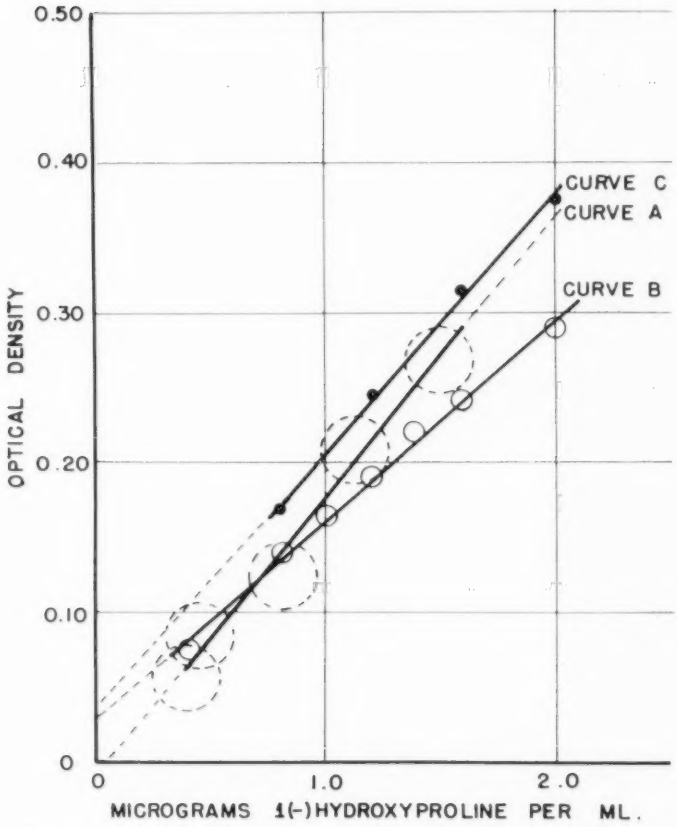

FIGURE 1.—Some hydroxyproline reference curves. (*Developed color measured at 560 millimicrons.*

which was carried out at 70°C. The data given in the third part of Table I and in curve *C* of Figure 1 were secured by the procedure outlined in this paper. The data secured from the original procedure represent measurements of the developed color made without dilution to constant volume, while the latter two sets of data represent color-density values read on the diluted colors. However, all data are presented as the color-density values resulting from a common concentration of hydroxyproline, expressed as micrograms per milliliter of the colored solution as read, so that they can be directly compared.

The within-level mean-square values in the analysis of regression tables at the bottom of Table I are particularly interesting. The square root of these values is an estimate of the standard deviation of the determination of

optical density in the three methods; thus, it is a measure of the precision of the three variations of the method. These standard-deviation values are 21.1 for data secured by the original procedure, 10.3 for data secured by intermediate procedure, and 5.1 for data obtained by the procedure given in this paper. These values have been used as radii in Figure 1 for the circles which indicate the average value for the optical-density equivalent to the varied, known amounts of hydroxyproline taken. The lines drawn through these circles are the linear relationships which the analyses of regression indicated to be the best for the data. The significant mean-square values due to "deviation" in the analyses of regression indicate that the latter two variations in the method, with their improved within-level precision, could be more exactly represented by a curved line. This line, whose concavity would lie toward the x-axis containing the level of hydroxyproline, would be used for very precise work; it would bring the extrapolation of the curve to zero concentration of hydroxyproline nearer to the origin of the axes, which point should lie on the curves since the developed colors were read against a reagent blank in all cases.

Baker, Lampitt, and Brown (1), Martin and Axelrod (8), Miyada and Tappel (9), and Grunbaum and Glick (4) have published articles which confirm the fact that improved precision in the original method is desirable. These four articles have retained the original Neuman and Logan practice of reading the undiluted color; the last method is however a micromethod using a 100-μl volume for the developed color. Comparison of the data reported in these four articles with that reported here must take this difference in dilution into consideration. The dilution of the developed color to 25 ml. lowers the acid concentration to a level intermediate between the two higher levels studied by Miyada and Tappel. Our results are consistent with their results indicating that the developed color is not stable with time but that a diluted acid concentration in the final colored solution improves the color stability. To minimize the effect of this color instability still further, our procedure standarizes the time elapsed between the time the colored solution is removed from the 70°C. and the time the color value of the diluted solution is read to 30 minutes.

Our work has confirmed the observations of Baker, Lampitt, and Brown (1) and of Grunbaum and Glick (4) which indicate that lower concentrations of hydrogen peroxide than those indicated in the original procedure are desirable. These two articles indicate a preference for 2% H_2O_2, while our procedure employing 1.8% H_2O_2 has given more color and better precision than we were able to secure with the original Neuman and Logan procedure. Our experience would not confirm the observation of Martin and Axelrod (8) that the presence of small amounts of iron to promote removal of excess hydrogen peroxide has a significant effect on the precision of the method; it seems probable that the agitation of the solutions is more important than

either the temperature or the presence of a specific additive to remove excess peroxide at this stage.

Our results do not confirm those of Miyada and Tappel (9) who found that the form of the optical density–time curves resulting from the use of color-development baths at 70° and 80° C. differ. Our results would confirm the shape of the 80°C. curve given in Figure 1 of the article by Miyada and Tappel, and we can find no logical explanation for their results at 70°C. Our results indicate that a temperature of 70°C. in a color-development bath gives a broader time interval during which values of optical density approximating the maximum may be attained, which should improve the precision of the results. The combination of 25 min. at 70°C. was selected for the conditions of color development because this combination gave maximum color development in a practical time and because the day-wise precision of the results was improved. Further, the lower temperature makes the water bath and the color-development tubes easier to work with, so that the practical advantages favor the use of the lower temperature for color development.

USE OF THE HYDROXYPROLINE METHOD ON CURED HIDE SPECIMENS

The precision of the hydroxyproline standard curves does not entirely establish the practical precision of the method as applied to the determination of leather-making substance. Some estimates of the practical precision of

TABLE II

THE TOTAL KJELDAHL NITROGEN AND HYDROXYPROLINE NITROGEN CONTENT OF CORIUM PREPARATIONS

Corium Preparation Number and % Moisture	Nitrogen (As-is basis) %			Average % Nitrogen (Dry basis)	% HPN/0.1068 / % TN × 5.62
	Day 1	Day 2	Day 3		
	Total Kjeldahl Nitrogen				
1	15.94	15.96	15.90		
12.4% H_2O	16.00	15.91	16.02	18.21	—
2	15.73	15.69	15.77		
13.4% H_2O	15.67	15.69	15.70	18.14	—
3	16.05	16.04	15.40		
11.2% H_2O	16.12	16.05	15.93	17.94	—
	Hydroxyproline Nitrogen				
1	1.08	1.13	1.08		
12.4% H_2O	1.10	1.13	1.11	1.26	0.115
2	1.02	1.10	1.05		
13.4% H_2O	1.09	1.03	1.11	1.17	0.108
3	1.09	1.12	1.14		
11.2% H_2O	1.11	1.08	1.07	1.24	0.115

the method have been secured by repetitive analyses on acetone-dehydrated steerhide corium splits and on specimens taken from salt-cured hides. These data comprise Tables II through V.

TABLE III

ESTIMATION OF THE PRECISION OF THE TOTAL KJELDAHL NITROGEN AND HYDROXYPROLINE NITROGEN DATA (STATISTICAL ANALYSES OF DATA OF TABLE 2)

Source of Variance	Degrees of Freedom	Total Kjeldahl Nitrogen (As-is basis) Mean Square	F-Value	Hydroxyproline Nitrogen (As-is basis) Mean Square	F-Value
Preparation	3 − 1 = 2	0.1112	6.35*	0.0054	4.50*
Day	3 − 1 = 2	0.0288	1.65	0.0009	0.75
PXD	2 × 2 = 4	0.0402	2.30	0.0017	1.42
Replication	3 × 3(2−1) = 9	0.0175	—	0.0012	—

Statistical Parameter	Total Kjeldahl Nitrogen (As-is basis)	Hydroxyproline Nitrogen (As-is-basis)
Average value	15.86%	1.09%
Standard deviation	0.132%	0.0346%
Coefficient of variation	0.86%	3.17%

*Significant at 5% level.

TABLE IV

APPLICATION OF THE ANALYTICAL METHODS RECOMMENDED FOR CURED HIDES TO SPECIMENS FROM TWO HIDE LOTS

Analytical Factor	Regular-Cure Hide Lot	Delayed-Cure Hide Lot
% *Chloroform-Extractable Fat*		
16-hour hydrolysis	5.82	5.31
	5.32	6.27
24-hour hydrolysis	5.17	7.71
	7.06	6.85
% *Total Kjeldahl Nitrogen*		
16-hour hydrolysis	7.01	6.98
	7.11	7.01
24-hour hydrolysis	7.26	7.04
	6.88	7.00
% *Hydroxyproline Nitrogen*		
16-hour hydrolysis	0.469	0.468
	0.467	0.456
24-hour hydrolysis	0.473	0.467
	0.476	0.468
Material Balance		
%Moisture (% wt. loss at 80°C. *in vacuo*)	40.94	40.19
% Ash (% residue after 16 hr. at 600°C.)	13.80	13.99
% Fat (average of above)	5.99	6.90
% Protein (% Kjeldahl N × 5.62)	39.51	39.95
Total	100.24	101.03

TABLE V

WEIGHT CHANGES IN HYDROXYPROLINE AND PROTEIN FROM FLAYING TO UNHAIRING

(Data based on 50 kosher steerhides split down backbone after flaying and made into two separate cure packs)

Stage in Process	Chloroform-Extractable Fat lb.		Hydroxyproline lb.		Total Protein (% N × 5.62) lb.		Lb. Hydroxyproline / Lb. Total Protein	
	Regular Cure	Delayed Cure	Regular Cure	Delayed Cure	Regular Cure	Delayed Cure	Regular Cure	Delayed Cure
(Average Hide Weight at Flaying—66 lb.)								
Fresh sides*	45	49	51	50	427	404	0.119	0.124
Cured sides*	85	84	46	45	415	408	0.111	0.110
Unhaired sides	52	40	51	52	406	390	0.126	0.133

*Data on fresh sides and cured sides based on analyses on butt-clipped and hand-fleshed specimens to give results comparable to unhaired side data.

Tables II and III present data secured from the examination of steerhide corium splits. Fresh steerhides were secured immediately after flaying, and the bend areas taken for preparation of the corium splits. The long hair was clipped (with clippers used in the preparation of hair-on leather) and the clipped, washed bends were fast frozen in the form of flat strips about 3" × 24"; these frozen strips were then fleshed and cut into a grain split and a corium split, using a fixed-blade sole-leather splitter. The data in this paper are concerned only with the corium splits. The thawed splits were washed with 8–10% NaCl solutions to remove any debris accumulated during splitting and to extract salt-soluble globular proteins from the cut surfaces of the pieces. However, no effort was made to extract the pieces exhaustively to prepare a highly purified collagen. Some deliberate differences were included in the preparation procedure; these differences will not be discussed further except to note that the second preparation would be expected to have a lower collagen purity. The washed or extracted corium was then water-washed to remove excess salt and defatted and dehydrated by successive passage through ethanol and acetone. Aeration to remove the acetone produced air-dry, white, supple corium splits which can be stored at ordinary humidities; portions of these corium preparations were ground in the Wiley mill to pass a 4-mesh sieve, yielding white, fluffy, fibrous products which served as the standard substrates used to secure the data given in Tables II and III.

Table II presents data on the total Kjeldahl nitrogen and on the hydroxyproline nitrogen secured when these three preparations were each analyzed randomly and independently on three separate days, employing the customary within-day replication. Since Table II contains only the raw data, no comment will be made except to note the lower ratio of hydroxyproline to total protein (last column of Table) for preparation No. 2, which would be expected in view of the lower purity of the preparation noted above. Table III presents the results of the statistical examination of the data in Table II. The known differences in the preparation procedures have been reflected by the fact that the effect of "preparation" has attained the 5% level of significance. The day of analysis and the preparation by day interaction effects have not attained the 5% level of significance for either method; this of course is a characteristic of an acceptable analytical method. The data in the bottom of Table III compare the precision estimates for the two analytical procedures, which estimates may be calculated from the data in Tables II and III. The standard-deviation figures given are the square root of the replication mean square appearing in the analysis of variance tables; standard deviation is a statistical measure of the dispersion of any measurement under consideration. It is noted that the standard deviation of the hydroxyproline determination is about one-fourth that of the customary Kjeldahl nitrogen determination; however, the coefficient of variation of the hydroxyproline

determination is almost four times that of the Kjeldahl nitrogen determination. Since the coefficient of variation is 100 times the ratio of the standard deviation to the mean, or average value, and since the mean for hydroxyproline is about 1/15 that for the Kjeldahl nitrogen, the above comparative estimates of the precision of the two methods are consistent. These estimates of precision of the two methods are considered satisfactory for analyses performed on biological materials, and these results indicate that the method does have practical possibilities. It may be noted that the coefficient of variation of the hydroxyproline standard curve was only 1.83%, so that a significant contribution to variability is inherent in the skin or hide specimen and not a characteristic of the method itself.

Tables IV and V present data secured when these methods were applied to cured hide specimens rather than to the standardized preparations. These data have been secured during the course of the curing studies reported by Hauck and Lollar (5); the regular-cure sides were subjected to salt-curing in the packing-plant hide cellar immediately after flaying, while the delayed-cure sides were alternate sides from the same hides that were allowed to lie in pile for 48 hours before curing them with used curing salt. Since the hydrolysis procedure has been developed on ground material, and since the cured hide specimens had to be added to the acid for hydrolysis in the form of small chunks which went into solution slowly, it was decided to compare the effect of 16 and 24 hours of hydrolysis.

Table IV presents data on the application of the methods discussed in this paper to specimens taken from these lots of cured hides. It is obvious that the two cure packs do not differ significantly in composition. The time of hydrolysis has not had a significant effect on the amount of total Kjeldahl nitrogen or on the amount of hydroxyproline nitrogen. The data on material balance given at the bottom of Table IV present the usual summation to approximately 100; the excess value over 100 is not surprising since our experience indicates that the customary factor of 5.62 to convert Kjeldahl nitrogen to total protein is too high for cured hide specimens.

Specimens were also taken from these hides at the freshly flayed stage and in the white, unhaired stage prior to baring. Table V presents comparative data on the composition of the sides at the three stages: after flaying, after curing, and after unhairing. Since this triplicate sampling of the same sides requires some dissimilarity of hide-sampling area, it should be expected that some differences between the three stages would be detected. The specimens from the freshly flayed hides and from the white, unhaired hides were taken near the root of the tail, while the cured hide specimens were taken further forward in the kidney area of the sides. It is therefore logical that the latter specimens should contain more grease, since the hides were taken from a kosher kill and were from well-nourished animals.

All data in Table V are calculated to the total pounds of fat, hydroxyproline, or total protein; these analyses involve the assumption that the analytical data secured from the specimens taken for analysis are representative of the total weight of the hides at each stage. This assumption is certainly somewhat erroneous; in particular, the specimens from cured sides were taken from the very greasy kidney area and would be expected to show a higher level of chloroform-extractable fat and a dilution of the protein. Table V shows this effect in the data given for fat and hydroxyproline. This limitation of the data in Table V must be taken into account in the interpretation of the data.

The excellent agreement between the pounds of hydroxyproline at flaying and after unhairing suggests that neither the tannery processing nor the curing variables have removed hydroxyproline to a significant extent. The data on total protein show the anticipated small decrease due to protein removal during brine run-off and soaking as well as during liming and unhairing. The ratios in the last two columns of Table V show that the collagen has been purified by the processing from flaying through unhairing. Since bating is known to remove additional noncollagenous protein, and since even bated hide contains such noncollagenous proteins as elastic tissue and globular proteins, it is not surprising that these ratios do not attain the value of 0.14 indicated for more highly purified steerhide collagen (9). However, these ratios do indicate that the earlier conclusion by Hauck and Lollar, (5) that the delayed-curing procedure has had small influence on the hide composition is correct. Considering the fact that these ratios must reflect the error of sampling as well as the errors in both methods of analysis, their general agreement seems satisfactory and indicates further that the hydroxyproline procedure does have potential value for use by tannery chemists.

CONCLUSION

Data have been presented which indicate that the hydroxyproline determination originally described by Neuman and Logan (10) can be modified in ways that are consistent with the observation of others (1,4,8,9) to improve the precision of the determination. It is indicated by the data presented on some analyses of hide corium splits and of specimens taken from hide lots after flaying, after curing, and after unhairing, that the method has potential value for the determination of leather-making substance.

This paper has not been concerned with the determination of the proper factor to convert hydroxyproline to leather-making substance. It may be recorded that Baker, Lampitt, and Brown (1) have proposed that factor 7.57 be used to convert hydroxyproline values to collagen in their studies of the connective-tissue content of meat. Hauck and Lollar (5) have used approximately this factor; however, it must be realized that it is probable that *pure*

collagen may contain an even higher level of hydroxyproline (9) and that a factor of about 7 might be more realistic.

Work is being continued in an effort to improve the precision of the results to a still greater extent. Our studies to date have not adequately covered the effect of the other amino acids resulting from the protein hydrolyzate on the precision of the assay. Baker, Lampitt, and Brown (1) have indicated that an increased level of cupric sulfate is desirable, especially when the ratio of hydroxyproline to other amino acids becomes small. More work is also indicated to evaluate the possibility of losses of hydroxyproline during hydrolysis. Wierbicki and Deatherage (13) have suggested a shorter hydrolysis time and the use of stannous chloride to minimize humin formation; this modification might be desirable on the hide specimens. Efforts are under way to write quality specifications on the reagents used in the method to the end that it may exhibit improved day-to-day precision. These various studies are still being carried out on the method; however, it seems desirable to publish the article at this time to indicate to the industry some of the potential value of this method in the determination of leather-making substance, in the hope that the publication will stimulate further work on the method.

ACKNOWLEDGMENT

This paper has summarized work carried out in our laboratory over a five-year period and presents data secured by many individuals. Particularly significant contributions to information reported here have been made by Dr. C. Deasy, Raymond Hauck, Miss Helen Steinle, Miss Betty Kiley, and Mrs. Margaret Anne Crawford. The support of the Tanners' Hide Bureau and of Leather Industries of America is also appreciated.

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DISCUSSION

JAMES M. CASSEL (National Bureau of Standards): Last evening at the Raw Stock Evaluation Committee meeting there was a great deal of good, sound discussion of a practical nature which could well be appended to this paper. Any approach to a correlation between raw stock and leather-making material is obviously worthwhile. The leather-making potential of a hide is dependent on the formed collagen fibers in the hide matrix. The amount of collagen fiber in the hide is about seven times the content of the amino acid hydroxyproline.

Dr. Lollar has discussed a method for the determination of hydroxyproline. A method such as this, to be of value in estimating leather-making potential, has to have high precision. This is, of course, independent of any sampling problems that are inherent in hide analysis. Dr. Lollar has shown that the coefficient of variation in his hydroxyproline colorimetric test is about three to four times that obtained on the ordinary Kjeldahl nitrogen test. Now, whether this inherent error in the test can be reduced further, or whether it needs to be reduced any more to be of value as a means of determining leather-making substance, is a question.

I have a few specific questions to ask Dr. Lollar before opening the meeting to general discussion:

(*a*) Did you use a spectrophotometer in this work rather than a colorimeter?

(*b*) Do standards need to be run simultaneously with the unknown? If run in duplicate (standard and unknown), how many test tubes at the most can you handle?

(Our experience using the original Neuman-Logan test indicates that only a limited number of individual measurements can be made within a given test run. I was curious as to whether you had any problems along this particular line.)

(*c*) One thing I may have missed in your presentation was the final color development at 70°C.—or was it at room temperature? Does the color hold pretty steady, or is there some fall-off in color yield with time?

(Actually, I have found that sometimes in developing the color at 70° and then cooling to room temperature, if you wait a while before you make your measurements, density continues to increase.)

(*d*) Another question I have is on the use of sulfuric acid for hydrolyzing, to set free hydroxyproline. Was there any reason for preferring that over hydrochloric acid?

DR. LOLLAR: With respect to the spectrophotometer for research purposes, we do use the Beckman DU spectrophotometer. However, I do know from actual trying it out, that you could use any good colorimeter with an interference filter, and there is no reason why it could not be done under tannery conditions.

With respect to the temperature at which the color was developed, we do still develop the color at 70°, and we have carried out our timing of the procedure in such a way as to read our developed colors at the maximum color attained. The details will be in the paper.

You will notice that in most of the cases there were four points on the standard curve, and we make it a practice every time we run a set of unknowns to run these four points and to compare them. In fact, essentially I maintain a control chart on my standard curve.

I have the analysis of regression limits around the curve, and if anybody falls out of that analysis of regression limits there is something wrong with his results, and the work has to be repeated. You must, in any colorimetric system—and in this above all—maintain painstaking and unremittingly precise control of your conditions. That is the reason I am not yet ready to say that it is something that I think can be used too easily under practical conditions.

We have used both hydrochloric and sulfuric acid interchangeably. We have used sulfuric acid more because we wish to use an aliquot of the hydrolyzate for Kjeldahl nitrogen.

MR. CASSEL: You mentioned that your color reagent is packaged under argon. Are you able to repeatedly use reagent from the same bottle?

DR. LOLLAR: We buy it mostly in 10-gram bottles and therefore do not have to have a bottle open too long. We do store it under refrigeration. However, I think that is merely an extra precaution, for safety's sake. Since we have been using this particular grade, we have had very little trouble. We have developed the interest of Mr. Green, Matheson Coleman & Bell production control chemist, and he is cooperating with me in assuring us that each lot that is prepared meets rigorous requirements for this particular method.

I think really we have more trouble with the normal propanol that is used to dissolve the reagent than we do with the reagent itself, and that is one of the things I want to study—how we might be able to better specify with normal propanol.

DR. JOHN H. HIGHBERGER (United Shoe Machinery Corporation): Did you have any experience with the Axelrod modification?

DR. LOLLAR: We have done no statistical comparison with the Axelrod modification. We tried it once when it was published. We did not find it any better under our operating conditions than we were doing with even our Method B, and decided not to develop it. We did find it to be better than the original Neuman and Logan—about the same as our Method B—and decided therefore to work further in our direction rather than in theirs.

DR. WILLIAM J. MCDERMOTT (Rohm & Haas Co., Philadelphia, Pa.): How do you test for the complete removal of peroxide? Or isn't it necessary to go to complete removal?

DR. LOLLAR: There is a lot of emphasis in the original article on the importance of that. We feel that it can be done satisfactorily by observing the nature of the bubble release as the solutions are vigorously shaken.

DR. MCDERMOTT: You get fairly complete removal that way?

DR. LOLLAR: If you shake vigorously and continuously until such a time as bubbles are no longer released, we do not find that the residual peroxide interferes in the precision of the result—at least to the limit that we reported there. These curves are based on runs of repeated usages over many days. Each one of the curves was based on about 100 degrees of freedom for the statistical analysis. So we have some confidence in the limits that we have placed on them.

DR. T. C. THORSTENSEN (Lowell Technological Institute, Lowell, Mass.): I would like to review briefly, for the information of the members here, the happenings of the Raw Stock Evaluation Committee last night with regard to this particular question.

Mr. Cassel has mentioned that we discussed the practical aspects of raw stock evaluation by methods such as this. The members of the Committee feel that such a method as Dr. Lollar has proposed, if it were of sufficient precision, would be very valuable but that at the present time the variation is too great to be used for hide evaluation.

However this work is very important for the development of a raw stock evaluation method, and I think he should be encouraged to continue this line of work. The precision should be very high to be of value, and for that reason we are not proposing this or any similar method as a means of hide evaluation at this time.

ANDREW SALAMATOV (Barrett & Company, Newark, N. J.): I noticed on all those charts that the ratio between the Kjeldahl figures and the hydroxyproline figures is approximately 1/15, and it remains constant. This being so,

what would be the advantage and the significance of the hydroxyproline method over the Kjeldahl method?

DR. LOLLAR: I mentioned that these particular preparations were attempts to prepare a standard leather-making substance. Because I was concerned with the precision of the method, I did not present many data on the actual application of the method to cured hides.

The ratio does vary with the conditions of the cured hides; and under those conditions, therefore, such things as the amount of hair, amount of manure, the amount of globular proteins as dependent on the sex and age of the animals, will vary the ratio. This method would give you the more directly leather-making substance in the hide lot.

The myriads of victims slain in Jewish sacrifices must have afforded the skin market a copious supply. The scarcity of glass, pottery and earthenware would, however, cause a constant demand for leathern bottles and drinking vessels, and these, by reason of climate, defective manufacture, and by exposure to the process of fermentation, were very perishable; perhaps even more so than the brittle vessels of glass and clay.

—*Leather Manufacture.* John W. Stevens. Chicago: The Shoe and Leather Review, 1890.

The National Association of Glue Manufacturers has instituted a research program at Brooklyn Polytechnic Institute covering the development of an improved adhesive based on hide and bone glues with the ultimate hope that this research will result in an extension of existing markets and an improved return to all related producers. The Glue Manufacturers' group has entered into closer liaison with NHA in order to prevent duplication of effort, and to exchange information which might be of interest to the respective membership of the two associations.

—*NHA Bulletin,* June 14, 1957.

After the successful production of chrome tanned goat skins, the tannage of calf, sheep and side leather rapidly followed. The name of Mr. E. L. White of the firm of White Brothers of Lowell, Massachusetts, should here be mentioned; who with courage and foresight hardly less than Foerderer's, developed box calf, the first successful chrome calf leather.

—*Lactic Acid In Leather Manufacture.* Alan A. Claflin and Harry P. Corson. Boston: The Avery Chemical Company, 1920.

In one way, indeed, chemistry must be admittedly unwelcome to the conservative tanner—it is the key to mysteries and has rediscovered and thrown open to the world many secrets which he believed safely locked within the doors of his factory! But even so it must be reckoned with, for, like the genii of the stories, it can neither be killed nor bound, but is fortunately the willing servant of all who have intelligence to use it; and as capable of discovering new secrets as of throwing open the old ones.

—*Leather Industries Laboratory Book.* H. R. Procter. London: E. & F. N. Spon, Ltd., 1908.

RATIO OF LIGNOSULFONATE TO VEGETABLE TANNIN TAKE-UP FROM BLENDS IN SOLE LEATHER TANNING*

JOHN DAVIS, RICHARD BENNING, and MARTIN BAUM

Marathon Corporation
Rothschild, Wisconsin

ABSTRACT

Fractionated sodium lignosulfonate was mixed with vegetable tans—wattle and/or quebracho—to give blends of approximately 10.75% total tannin, of which 35% was lignosulfonate. Bated heavy hides were immersed for 15 days in these blends at a temperature of 95° F. Liquor pH was adjusted between 3.0 and 3.7 at the start and after the first five days of each cycle.

The liquor was refortified to approximately 10.75% tannin as based on sap liquor analyses, and the tanning cycle was repeated until six cycles were run on each blend.

Analysis of new and refortified liquors showed that ratio of tannin methoxyl to tannin content and ratio of lignosulfonate to vegetable tannin as determined by paper chromatography remained constant throughout the six cycles. These results therefore indicate that fractionated sodium lignosulfonate is taken up by hide in the same ratio that it is present in the original lignosulfonate-vegetable blend.

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INTRODUCTION

Lignosulfonates are widely used in the production of upper leather and have gained limited acceptance in the tanning of sole leather. Lack of complete acceptance is perhaps due to the general knowledge that sole leather made with 100% lignosulfonate does not have the properties and character associated with all-vegetable-tanned sole leather. Thus, some tanners are reluctant to use lignosulfonates in significant amounts in their vegetable blends because of fear of incomplete take-up by the hide. Incomplete take-up could bring about an accumulation of tannin which might ultimately result in "slack tannage", poor color, reduction in yield, and poor leather quality.

*Presented at the Fifty-third Annual Meeting of the American Leather Chemists Association, Lake Placid, New York, June 2-5, 1957.

It was determined to resolve the problem whether or not lignosulfonate remained in its same ratio to wattle and/or quebracho throughout an extended tanning period when blends were employed in the tanning of heavy bated hide. The lignosulfonate was present in a significant amount, i.e., 35% of the total tannin in the blend.

PROCEDURE

Tanning extracts and blends.—Three tanning liquor blends were used and all made up to approximately 10.75% total tannin as determined by official ALCA methods.

Raw tanning extracts were solid wattle, spray-dried solubilized quebracho, and sodium lignosulfonate. All blends were made up on a tannin basis to contain: Blend No. 1, 65% wattle and 35% lignosulfonate; Blend No. 2, 65% quebracho and 35% lignosulfonate; and Blend No. 3, 32.5% wattle, 32.5% quebracho, and 35% lignosulfonate.

The pH of blend was adjusted by addition of dilute phosphoric acid. One-half to one percent sodium bisulfite was added to reduce insolubles.

Hide used and sampling plan.—Two single matched bends, after bating, were cut in half parallel to the line of the backbone, and hide blocks measuring 6½ x 9½ inches were taken from the shoulder and butt areas on the top half of each single bend (Figure 1). The top half of the bend is that part which extends from the backbone to a point approximately halfway to the belly edge of the bend. These hide blocks were cross-mated from each single bend to form a single "pack" weighing approximately 600 grams. Packs from the top half of each single bend were used in all blends of the first tan cycle, and similar packs made up from the lower halves were used in all blends of the second tan cycle. This alternate system assured that every other tan cycle would contain hide blocks from the top or bottom half of each single matched bend and that no particular hide area would be favored continually throughout the total period of six complete tan cycles. Bated hides were obtained from the tannery at timed intervals to coincide with the 15-day tan cycle. Excessive storage before use was thus eliminated. During the few days lapse of time between receipt and use hides were preserved in 2% borophenol solution at 70° F.

Tan cycle procedure.—Sodium lignosulfonate obtained by fractionating pulp-mill sulfite spent liquor with lime was blended with wattle and or quebracho to give tanning blends of approximately 10.75% total tannin, of which 35% was lignosulfonate. Bated heavy-hide packs, after having been soaked in weak rinse liquor for two days at 95° F., were immersed in the tanning blends for 15 days at a temperature of 95° F. The first weak liquors used to start off the tanning cycles were made by diluting a portion of each

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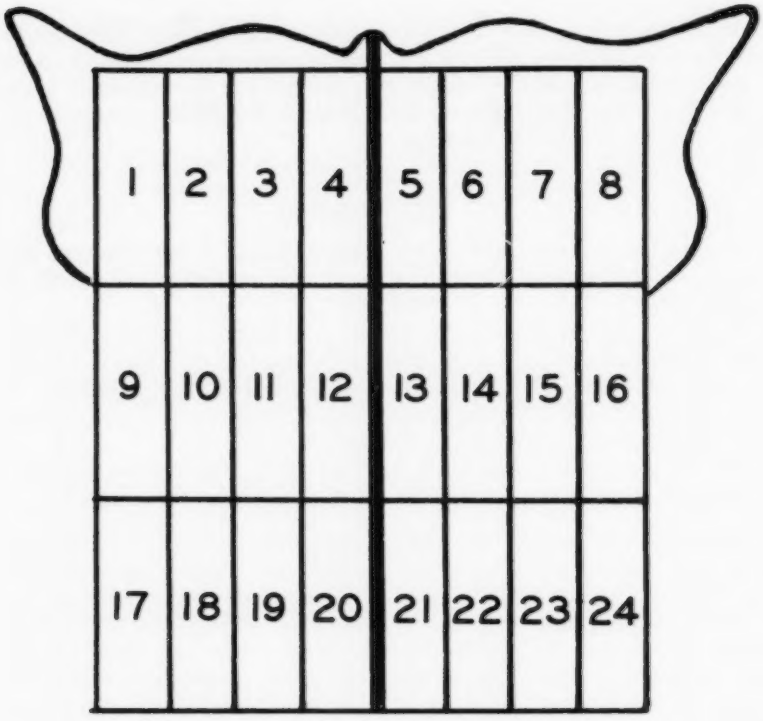

FIGURE 1.—Hide sampling plan.

	1st Cycle	2nd Cycle	3rd Cycle	4th Cycle	5th Cycle	6th Cycle
Blend No. 1	4–22	2–24	6–12	8–10	11–21	16–18
Blend No. 2	6–12	8–10	11–21	16–18	4–22	2–24
Blend No. 3	11–21	16–18	4–22	2–24	6–12	8–10

blend to approximately 1% solids with tap water. The pH was adjusted between 3.0 and 3.7 with dilute phosphoric acid at the start and after 5 days tanning time in the blends. No strengthening was done during the 15-day tanning cycle, and no liquor was sewered at any time. The tanned hides were removed at the end of 15 days in the blends and placed in plain tap water at 95° F. for a period of two days before being bleached, wrung, hand-oiled, and air-dried. The rinse of "sour water" thus obtained over the two-

day leaching period was used for the succeeding fresh-bated hide pack. The sapped blend from each tan cycle was refortified to approximately 10.75% total tannin in the same ratio of lignosulfonate and vegetable extract as originally made up, and the tanning cycle was repeated until six cycles were run on each blend. The ratio of liquor blend to hide was approximately 5:1. Neither liquor nor hide was agitated during the tan cycle.

This closed-system, single-vat method is not in general use today for heavy leather. However, we used this system because it reduces tannage time so that liquor equilibrium is obtained more rapidly than is possible in the conventional press-over system.

The tanning system was evaluated by (1) determining tannin and purity of all raw extracts and new, refortified, and sapped blend liquors according to official ALCA methods, (2) determining methoxyl on all raw extracts and new, refortified, sapped blend liquors, and on nontannin portions of these extracts and liquors, and (3) preparing paper chromatograms on new blend liquors at the start of the first tan cycle and the end of the sixth tan cycle.

RESULTS AND DISCUSSION

Analyses of raw tanning extracts and new blends are given in Table I and Table II.

Complete hide penetration by all three blend liquors occurred within seven to ten days from the start of each tan cycle. The rate of penetration was greatest with quebracho-lignosulfonate, and least with wattle-lignosulfonate. There was no evidence of grain "case-hardening" or plugging in the strong liquors. The color and leather yields remained good throughout all tan cycles and for all blends.

TABLE I

ANALYSIS OF MATERIALS USED (ALCA METHODS)

	Solid Wattle Extract	Spray-dried Quebracho Extract	Fractionated Sodium Lignosulfonate
Total solids	91.29	88.83	93.75
Soluble solids	89.25	87.69	93.27
Insolubles	2.04	1.14	0.48
Nontannin	19.10	13.60	39.52
Tannin	70.15	74.09	53.75
Purity			
Tannin/solubles	78.6	84.4	57.6
Tannin/solids	76.8	83.4	57.3
pH (analytical solution)	5.05	5.50	3.80

TABLE II

COMPOSITION OF FRESH BLENDS

	Blend No. 1 (65% wattle 35% lignosulfonate)	Blend No. 2 (65% quebracho 35% lignosulfonate)	Blend No. 3 (32.5% wattle 32.5% quebracho 35.0% lignosulfonate)
Total solids	16.21	15.15	15.71
Soluble solids	15.93	14.99	15.56
Insolubles	0.28	0.16	0.15
Nontannin	5.05	4.44	4.78
Tannin (actual)	10.88	10.55	10.78
Tannin (theoretical)	10.62	10.43	10.51
Purity			
Tannin/solubles	68.3	70.4	69.3
Tannin/solids	67.1	69.7	68.7
pH (analytical solution)	3.40	3.50	3.45
pH (straight extract)	3.00	3.00	3.00

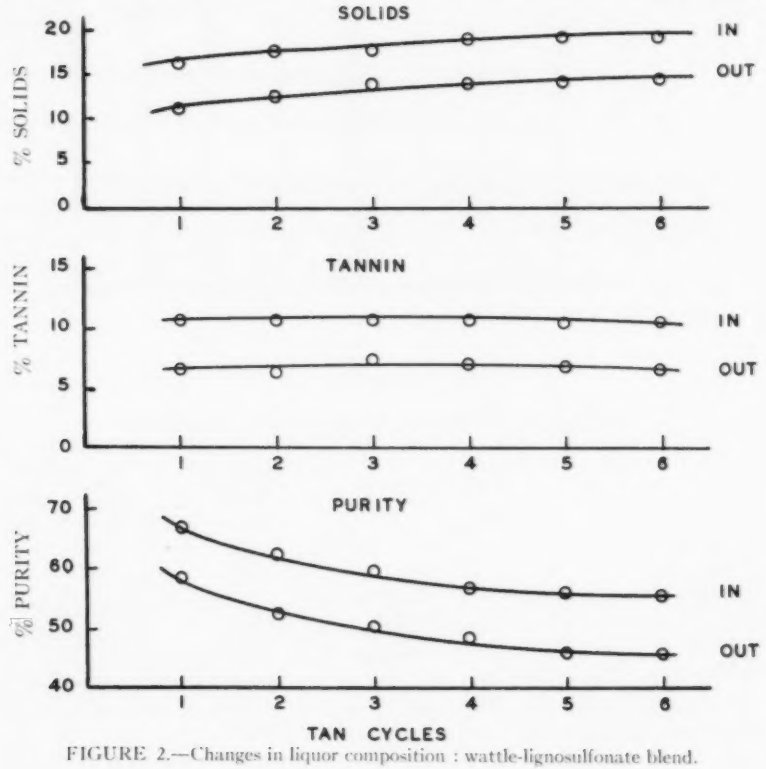

FIGURE 2.—Changes in liquor composition : wattle-lignosulfonate blend.

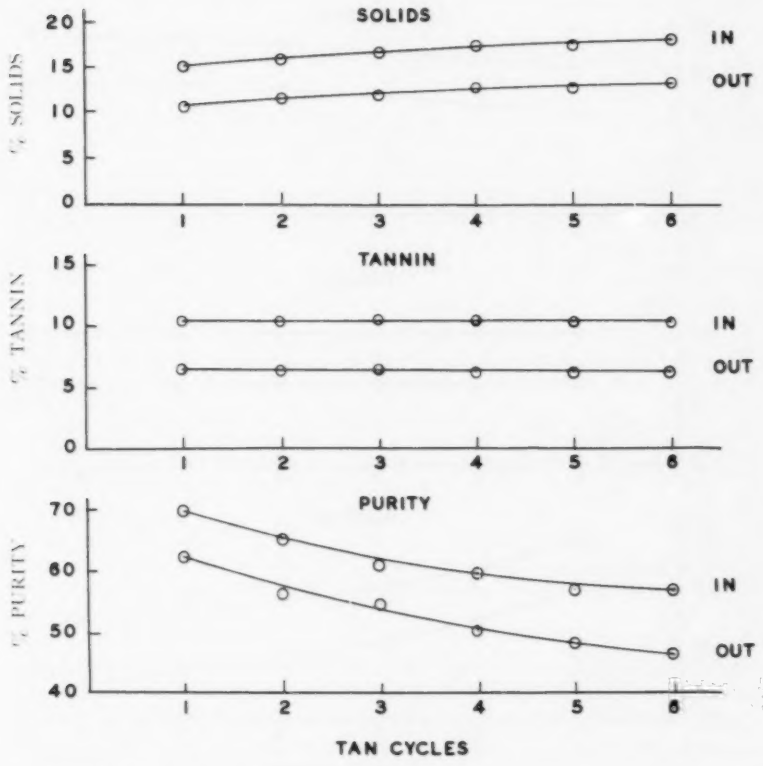

FIGURE 3.—Changes in liquor composition : quebracho-lignosulfonate blend.

Analyses of the new, sapped, and refortified liquors for the six complete tan cycles are given in Figures 2, 3 and 4. Liquor solids of both refortified and sapped liquors gradually increase with each tan cycle. This is to be expected since no liquor was sewered and sapped liquors were refortified back to original tannin content. The tannin content of liquors in and out remained constant, showing that a constant and uniform amount of tannin was taken up by the hide in each cycle. The purity, or ratio of tannin to solids, decreased with each cycle. This is due to sappage of tannin by the hide and gradual increase of nontannins. The values level off indicating that "equilibrium" is being approached by the end of the sixth tan cycle. Since nontannins are continually introduced by extracts and hides, it is only natural that a small and gradual decrease in purity results as the number of tan cycles increases.

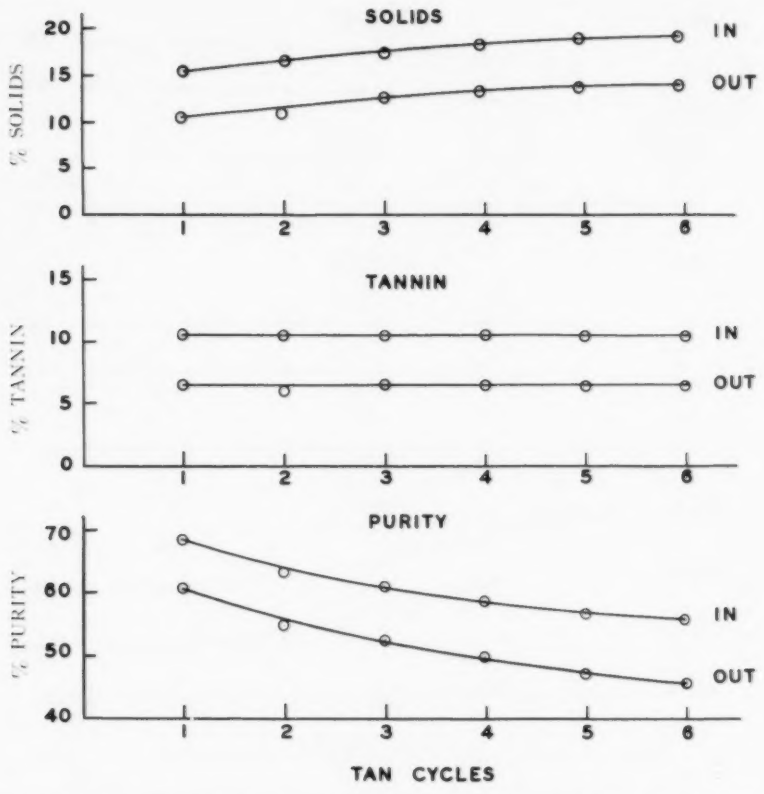

FIGURE 4.—Changes in liquor composition : wattle-quebracho-lignosulfonate blend.

The curves are remarkably alike, thus indicating that different blend composition has little effect on the analytical results.

Data on tannin utilization, Figure 5, show that 80% of the total tannin on a cumulative basis is utilized over a period of six tan cycles. There is no significant difference in tannin utilization among the three blends.

Methoxyl content as a measure of lignosulfonate in solution—It was obvious at the outset of this experiment that a method of differentiating between vegetable tans and lignosulfonate was necessary. One significant characteristic difference is their methoxyl content. All blend components were analyzed for total, nontannin, and tannin methoxyl content (1), and these values are given in Table III.

TABLE III

METHOXYL CONTENT OF EXTRACTS AND BLENDS

(Dry Basis)

	Total Methoxyl %	Nontannin Methoxyl* %	Tannin Methoxyl %
Wattle	0.95	0.58	0.37
Quebracho	0.95	0.17	0.78
Sodium lignosulfonate	12.3	1.4	10.9
Blend No. 1			
Start of 1st cycle	5.05	0.66	4.39
Start of 5th cycle	5.16	1.02	4.14
Blend No. 2			
Start of 1st cycle	5.25	0.48	4.77
Start of 5th cycle	5.57	0.67	4.90
Blend No. 3			
Start of 1st cycle	5.22	0.59	4.63
Start of 5th cycle	5.22	0.84	4.38

*Determined on nontannin from Waring Blendor modification of official ALCA method.

Analysis of these data shows that the tannin methoxyl content of fractionated sodium lignosulfonate is about 30 times that of wattle and 14 times that of quebracho. Because of these great differences, any accumulation of lignosulfonate tannin in the system would result in a significant increase in the methoxyl content of the tannin after several cycles. Table III gives the methoxyl analysis of each tanning blend at the start of the first cycle and the beginning of the fifth cycle. These data show only a slight difference in the tannin methoxyl content after four complete cycles, indicating that the lignosulfonate is being utilized to the extent it is present in the tanning blend.

Tannin methoxyl was determined after the fourth tan cycle because equilibrium as indicated by tan purity was fairly well established at this point.

A further illustration of this utilization of lignosulfonate is shown in Figure 6. This graph represents what would have happened to the tannin methoxyl content at the start of the fifth tan cycle if only part of the lignosulfonate added had been utilized. Lines are drawn at the tannin methoxyl content obtained experimentally and show a utilization of slightly over 100% for blends of lignosulfonate-wattle and lignosulfonate-wattle-quebracho, and 96% for the blend of lignosulfonate-quebracho.

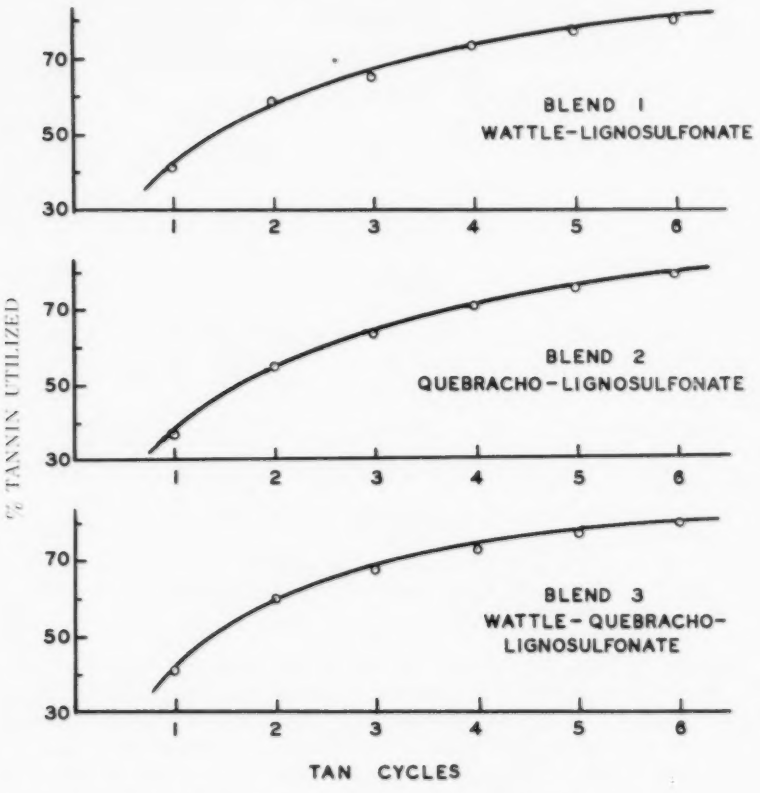

FIGURE 5.—Percent of total tannin in the system that is utilized.

Chromatographic and ultra-violet spectrographic examination as a measure of lignosulfonate in solution.—As a second method for determining whether either the vegetable or lignosulfonate components of a blend are preferentially absorbed by hide, we analyzed the liquors by means of paper chromatography (2). Known quantities of the original blends and sapped liquors from the sixth cycle were applied as strips on Whatman No. 1 paper (8 x 21 inches). The chromatograms were developed by downward flow with n-butanol – acetic acid – water mixture in the ratio of 4:1:5 for twenty hours. The papers were dried, and the fluorescent bands as distinguished by observation under short-wave ultraviolet light were marked. These fluorescent chromatograms, Figure 7, together with fluorescent chromatograms made on the individual blend components showed that each of the components or tanning materials that

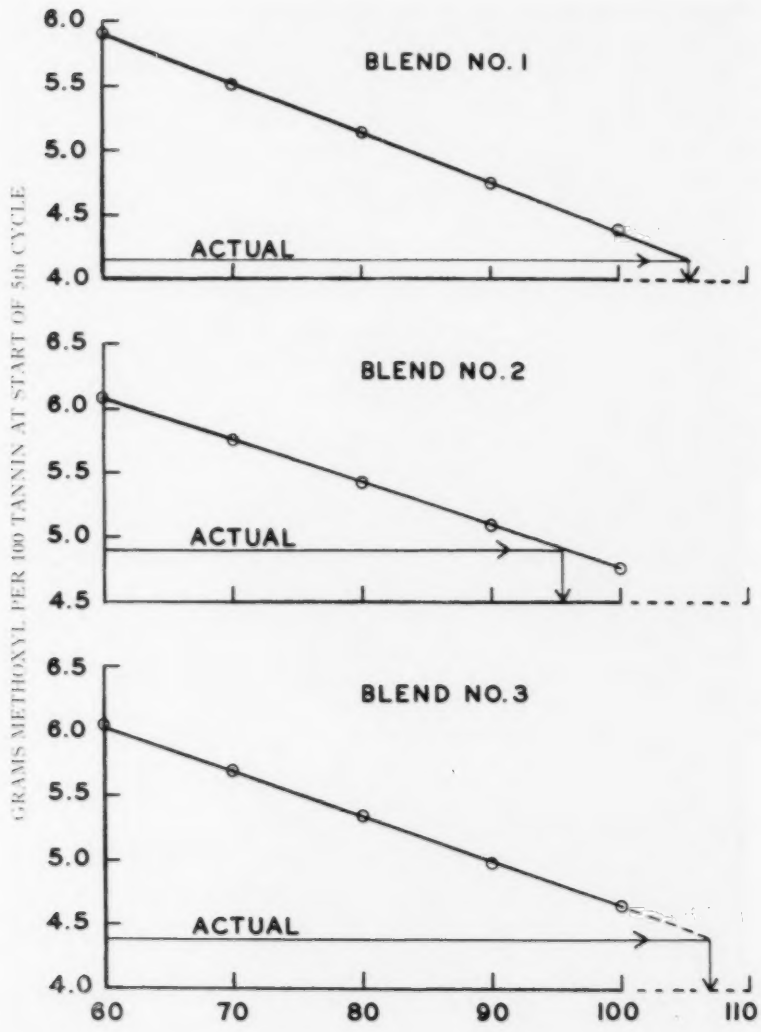

FIGURE 6.—Relation between tannin methoxyl and percentage of lignosulfonate tannin that is utilized.

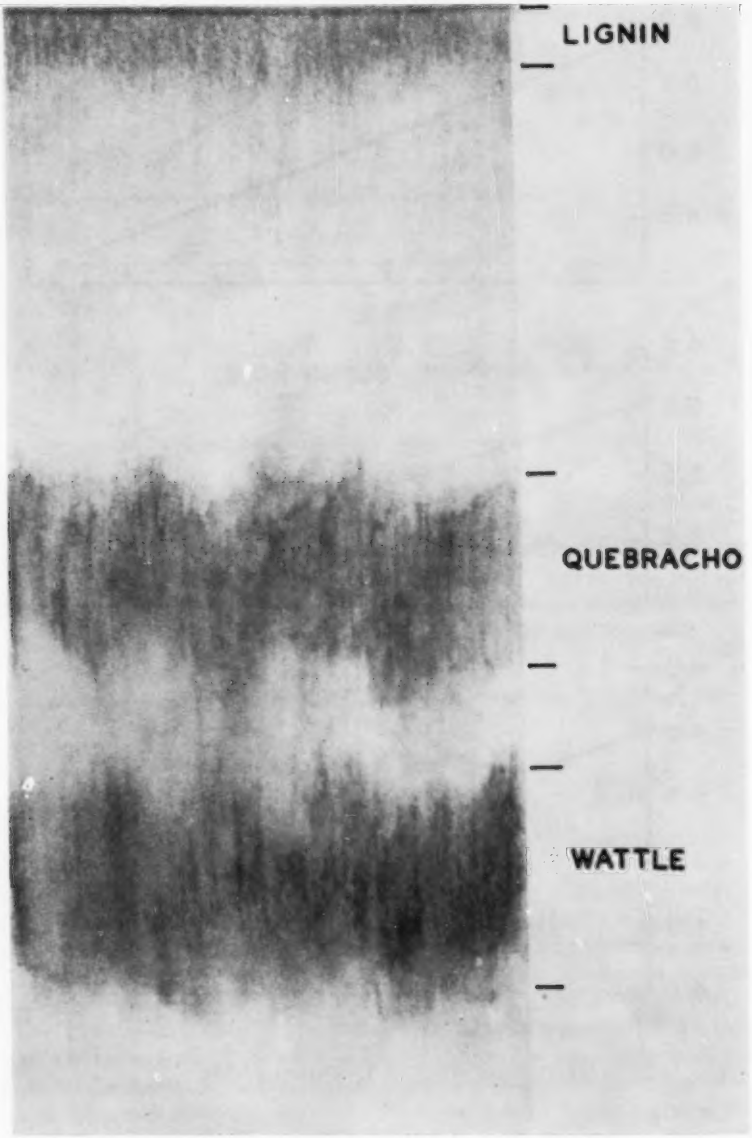

FIGURE 7.—Part of chromatogram of Blend No. 3 showing characteristic fluorescent bands.

we used gave its own characteristic band.* As a result, the individual components of a blend could be separated from each other. The separated bands as distinguished and marked under ultraviolet light were cut out from the chromatogram, extracted with a known amount of water, and their optical density was determined by measuring absorption at 278 mμ on a Beckman ultraviolet spectrophotometer. The ratios of K values (relationship between optical density and concentration) were then calculated. These values are given in Table IV.

TABLE IV

RATIO OF K VALUES OF FRACTIONS SEPARATED BY PAPER CHROMATOGRAPHY

Blend	Ratio of K Values Original Blend	Vegetable Lignosulfonate Sapped Liquor 6th Cycle
Wattle-lignosulfonate	0.230	0.224
Quebracho-lignosulfonate	0.102	0.115
Wattle-quebracho-lignosulfonate	0.301	0.316

Although this method is not precise, our results do show that the ratio of K vegetable tanning material to K lignosulfonate in the sapped liquors from the sixth cycle is essentially the same as the ratio in the original blend. These results indicate that there is no preferential take-up of either vegetable tannins or lignosulfonate by hide substance when tanned with blends of lignosulfonate and wattle or quebracho.

CONCLUSIONS

1. Lignosulfonate blended with either wattle or quebracho tanning materials is taken up by hide in the same ratio that it is present in the blend.

2. The closed system, single-vat tannage method is readily adapted to tanning studies. The liquors approach equilibrium in a comparatively short period of time. A minimum of raw materials is used. These factors plus the simplicity and ease of operation and control indicate that this system should be considered for large-scale tannery use.

*Quebracho, wattle, and lignosulfonate do not migrate as single bands in paper chromatography, but each has a band that shows up especially strongly under shortwave ultraviolet light. These bands have different Rf values and do not overlap. Figure 7 does not represent the whole chromatogram or the front of the chromatogram. It shows the highly fluorescent bands, which have the same Rf values as the bands in chromatograms made with the separate materials.

REFERENCES

1. Clark, E. P. *J. Assoc. Official Agr. Chemists*, **15**, 136, (1932).
2. Lederer, E., and M. *Chromatography* (Houston and New York: Elsevier Press, Inc., 1954).
3. Baum, M., R. C. Camp, and J. R. Salvesen. *JALCA*, **49**, 281 (1954).

Received June 28, 1957.

DISCUSSION

ARTHUR N. KAY (Howes Leather Company): It is seldom that we are treated to a paper with such practical overtones as this. Those of us who know Mr. Davis and Mr. Baum, know they do a very careful job in all of their work, and this is no exception. However, I should like to take issue a little with them over the seriousness of their claim that their paper indicates that lignosulfonates are not taken up differentially. I think we should be a little careful about that.

The figures indicate, to me at least, that they are correct in their assumption as far as their experimental conditions go. We must remember, however, that they are using a system—a tanyard system—that is very different from the conventional type. With these strong liquors, as we all know—take straight quebracho, for example—if we put a white hide into a 50-degree liquor, we get casehardening. If we put it into an 80-degree liquor, we get no casehardening, and tannage proceeds normally. There is a change in behavior. And in the stronger solutions the total solids of the blend appear to be absorbed, so to speak, *in toto*. Therefore, you would not expect a differential take-up, necessarily, under the present conditions. It might not hold in a conventional system.

That is not really a criticism. It is just a word of caution. By the same token, when Mr. Davis says that there is no sewering from the system, that is not exactly true because some of the solids will go into the rinse water. If we assume that the total solids are picked up *in toto*, then some of those solids will go into the water solution, and you have an actual sewering from the system because that is discarded. And you will reach equilibrium—I would say he reached it at about the fourth or sixth cycle.

On the other hand, the advantages of the system are as Mr. Davis mentions. It may well be this is the type of system that is needed and can be used when you wish to use high concentrations of lignosulfonates in the blend.

The other point that struck me as particularly interesting was the use of chromatography as a means of determining the presence of lignosulfonates in the blend. The Tannin Analysis Committee has done quite a lot of work on that—Mr. Jany and Mr. Dahl in their Subcommittees—and we have had no luck with chromatography. But this method offers promise, and I should

like to recommend to the Tannin Analysis Committee that they might consider it.

I am rather disappointed that we have no information on the leather produced—chemical analysis and physical characteristics, such as Mr. Kenzie showed us this morning. This is an omission that I am sure Mr. Davis will rectify.

ROBERT A. PLAW (Stahl Finish Co., Montreal): Is the penetration into the hide the same in the fourth or fifth cycle as it is in the first?

MR. DAVIS: We watched the penetration carefully and I, for one, was looking for greater penetration as the tan cycles increased, because the tan solids were increasing and we figured our osmotic pressure would give us increased penetration. However, we noted no differences in the rates of penetration throughout the tan cycle. They remained the same even though the solids at the beginning were around 15% and at the end of six cycles 19%.

HERBERT HODUS (Ohio Leather Company): In your statistical designing system how did you determine the number of specimens to use, and how many did you use?

MR. DAVIS: For each of three blends we cross-mated two specimens to form a single pack.

MR. HODUS: Do you think that is enough to make an honest statistical evaluation?

MR. DAVIS: Maybe I ought to go into this a little more. We thought we covered the hide pretty well (see Figure 1) for this reason:

In Blend No. 1 we took 4 and we cross-mated that with 22. This is from the top half of the single matched bend. Now for Blend No. 2, we took 6 and cross-mated that with 12. And then for Blend No. 3, we cross-mated 11 with 21.

For the second tan cycle we took specimens from the butt and shoulder areas of the lower half. But when we started the third cycle, we pushed the hide packs forward each one blend. Therefore when we ended up with the complete six tan cycles, all three blends had hide blocks from both the lower and upper halves and were cross-mated with specimens from each single matched bend. We did not take just one bend. It took more than that.

I thought it was a pretty good representation of the whole hide area. I don't know how you would run it out statistically, however, to be perfectly frank.

MR. HODUS: Did you compare sample 6 with 12, for example? Did you look at 6 and say that 6 is better than 12?

MR. DAVIS: No, we have not analyzed these samples yet. So we have no analytical data on the leather. The only data we have on the leather are the yield figures. We stated that the yield and color were good throughout the complete series of 6 tan cycles. That is all we know. We have ground up the leathers, though, and we are getting ready to analyze them. But we do not have those data yet.

Our primary purpose in this paper was to determine whether or not the lignosulfonate was going in with the vegetable extracts. That was our main point of interest.

MR. BALFOUR (Lignosol Chemicals, Quebec): Did the matched pairs all proceed simultaneously, or did you have to put some of these in storage?

MR. DAVIS: No, we did not store them. We ordered them at spaced intervals so that we would get them direct from the tannery. They were all treated that way, so that none was held over.

MR. BALFOUR: None were confused by introducing them during pickling?

MR. DAVIS: No.

MR. KENZIE (Ontario Research Foundation): Have you conducted countercurrent experiments to determine reabsorption of the tannin?

MR. DAVIS: No, we have not.

A type of journal of chemical interest showing still further specialization is the journal devoted to some specific industry, the conducting of which involves chemistry and chemical engineering. There are journals, in some cases many of them, for practically all of the large industries involving chemistry, as the petroleum journals, the paper journals, the dye journals and the rubber journals. Some of these are published by organizations of scientific and technical men interested in the industries involved, for example the *Journal of the American Leather Chemists' Association* and the *Journal of the Society of Dyers and Colourists*. These industrial publications sponsored by societies are usually filled with original papers, with sometimes sections devoted to abstracts, the papers being many times close to if not indeed pure science products.

—*A Guide to the Literature of Chemistry*. E. J. Crane and Austin M. Patterson. New York: John Wiley & Sons, Inc., 1927.

LIFE LINES

Brief Biographies of Our Contributors

MARTIN BAUM received his degree of chemistry in 1935 from the University of Wisconsin. Since then he has been employed in the Research Department of Marathon Corporation, conducting research on the recovery and utilization of lignosulfonates. At present he is supervisor of the wood and lignin research section.

RICHARD BENNING received his B.S. and M.S. in chemical engineering from the University of Notre Dame. He was employed one year at Reilly Tar and Chemical Company prior to serving two years in the Navy. Since November, 1947, he has been employed in the Research Department of Marathon Corporation where he is now leader of the group studying process and product development in the utilization of lignosulfonates.

JOHN DAVIS entered the leather and tanning extract industry in 1934. Prior to joining the Marathon Corporation in 1955 he was employed by the United States Leather Company 7 years, Armour Leather Company 3 years, American Extract Company 7 years, and National Bureau of Standards (Leather Section) 3 years. In the Marathon Corporation Mr. Davis is Senior Research Chemist in the field of lignosulfonates for the tanning industry. He has studied at Penn State and St. Vincent Extension College.

ROBERT M. LOLLAR—See the July issue of *JALCA*.

Before the time of Schultz, there were two anticipations of his invention [chrome tannage]. As far back as 1858, Professor Knapp, a German chemist and student of leather chemistry, had prepared some chrome tanned leather using a one bath solution, and in 1879 Heinzerling had patented a somewhat similar process for chrome leather, but these processes did not attract attention equal to that given to the process of Schultz, probably because until about the time of the Schultz patent, bichromates were scarce and high in price. The growing demand for bichromates for mordanting the alizarine colors in the textile trade, however, increased their production and lowered the price.

—*Lactic Acid In Leather Manufacture*. Alan A. Claflin and Harry P. Corson. Boston: The Avery Chemical Company, 1920.

In the earlier days of chemistry in America a number of chemists in the United States made it a practice to publish their papers in German journals, a tendency which has just about died out since the beginning of the twentieth century.

—*A Guide to the Literature of Chemistry*. E. J. Crane and Austin M. Patterson. New York: John Wiley & Sons, Inc., 1927.

ALCA NEWS

Proceedings, Reports, Notices, and News

of the

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The officers and Council of the Association join the editorial staff in extending to all members the warmest of season's greetings and sincere wishes for a happy, prosperous, and peaceful New Year.

MORE SOUVENIRS OF ROME

The Weldons and Stublaingses join friends leaving St. Peter's.

At the banquet (*clockwise from the left*): the Boraskys, Merrills, Mrs. W. L. Barrett, and the Salamatovs.

MINUTES OF THE MEETING OF THE COMMITTEE ON MEASUREMENT OF WATER RESISTANCE

(Section IV, Subcommittee III, Joint ALCA-ASTM Committee on Leather)

The meeting on October 17 in Cincinnati was attended by 23 members. The following items were discussed:

1. *Sole leather.*—Dr. Kanagy presented a sketch of a machine which he has been using to determine the resistance to water penetration. He obtained values in the range of 87 minutes for untreated finished leather up to 530 minutes for Orinite-impregnated leather. The machine is to be loaned to other laboratories so that standard samples of various leathers may be tested and the results correlated.

In addition, the Chairman will see that the present ALCA method for static water absorption is written up in the proper fashion and submitted to the ASTM.

2. *Garment leather.*—Dr. Chouinard reported that his group had found the Spray Test acceptable as a measure of surface repellency and agreed to write this up for submission to the committee.

He reported that they felt that an absorption test of some nature was also required and that they had obtained poor correlation with various shaker tests due to mechanical differences. They are now investigating the static absorption of whole skins, which seems to give good correlation so far.

He also described the Accelerotor as a possible test method, but further refinements will have to be worked out.

3. *Glove leather.*—C. W. Mann reported that they have obtained good correlation of the Tap Tester with the wet brick course and that further work will be completed with samples of leather which have been subjected to a standard treatment.

4. *Upper leather.*—The Chairman submitted a tabulation of the test results obtained on 3 samples each of 9 different leathers submitted to 11 laboratories for test by 7 different methods. All the results were received with one exception. The water-absorption values were received but not tabulated due to the fact that these were obtained only at the point of failure. Since a specimen failing at 100,000 cycles would naturally absorb more water than a specimen failing at 300 cycles, these figures were obviously unrealistic.

It was noted that a particular leather which resisted penetration to a high degree on all the flex-testing machines performed very poorly on the Tap Tester. Mr. Mann suggested that the probable explanation for this was the fact that the load applied to this particular leather was too high for this type

of leather. He described another test in which various leathers were carefully cemented into the vamp area of a test shoe and these shoes worn in a polyethylene over-boot containing water. The leather mentioned above performed satisfactorily in this test.

It was apparent that the flex-testing machines were essentially in agreement in that the well-treated leathers gave good values and the poorly treated leathers gave poor values with all the mediums. It was pointed out that a single test area of a highly water-resistant leather will occasionally give a low value and it is practically impossible to test enough samples to apply a statistical evaluation.

In view of the above, it was moved and passed that the Maeser machine, as defined in Method E-31, be modified to include automatic end-point detection as described in the ALCA *Journal* of July, 1956, and its speed increased to the range of 180–200 r.p.m., and the method, so modified, submitted to ASTM.

The meeting adjourned.

R. G. Ashcraft, *Chairman*

INTERNATIONAL UNION OF LEATHER CHEMISTS SOCIETIES FIFTH BIENNIAL CONFERENCE

Rome, September 15–20, 1957

The Conference was attended by about 550 people, including about 150 ladies, representing 19 countries. Forty Americans were present, including 20 members of ALCA. Worthy of special note was the presence of a number of chemists from the U.S.S.R. and Soviet-dominated countries, including such well-known figures as Kubelka, Masner, Stather, and Mikhailov.

On the evening before the official opening of the Conference, a reception was held by the Associated Italian Tanning Extracts Manufacturers, in the Grand Hotel, Rome. Visitors to the Conference were welcomed by Comm. berto Durio and Baron Dr. G. Zerilli-Marimo, who in his address placed the accent on the defense of the industry against the attacks of the leather substitutes. Dr. Turley, President of the International Union, replied to these addresses on behalf of the guests.

BUSINESS AGENDA

The Council of Delegates met on three occasions during the week to discuss the formal business of the Union. Among these matters were the acceptance of an invitation from the German Society to hold the Sixth Biennial Confer-

ence in Germany in 1959; the formation of a joint committee with the International Council of Tanners to help to publicize and improve leather; the admission as members to the Union of the Czechoslovakian Leather Chemists Society; the decision to present a memorial lecture at the 1959 Conference to commemorate the work of Arthur Harvey in promoting the present International Union; and the election of the 1957–1959 Executive Committee.

The elections resulted as follows:

President	Dr. G. A. Bravo (Italy)
1st Vice President	Prof. W. Grassman (Germany)
2nd Vice President	Dr. H. G. Turley (U. S. A.)
Co-opted Members	Dr. P. J. van Vlimmeren (Holland)
	Sr. M. Paniker de Pelach (Spain)
Hon. Treasurer	Prof. D. Burton (Gr. Britain)
Hon. Secretary	George Forsyth (Gr. Britain)

Monday, September 16

The Conference was officially opened in The Congress Rooms, Via Giolitti, with Dr. H. G. Turley (President of the International Union) in the chair. After a short address of welcome from Comm. Eberto Durio, Dr. Turley gave his Presidential address in which he reviewed the development and growth of such international conferences. He went on to describe the position of the industry today "faced with increasingly aggressive high-grade competition from the use of substitute materials" and the necessity of building a sound and solid bridge from theory to practice to enable the industry to meet these attacks.

Dr. Turley asked the meeting to stand in silence as a mark of respect to the memory of those members of the Union who had passed on since the last Conference. He mentioned as foremost among them Gustave Colchen, B. M. Das, F. G. Donnan, Arthur Harvey, R. O. Page, and Dean Williams.

The President then called on Prof. P. Chambard to present the Meunier Memorial Lecture, "The Life and Work of Prof. Louis Meunier."

Dr. Turley introduced Prof. J. B. Speakman, D.Sc., F.R.I.C., F.T.I., (University of Leeds) to give his lecture on "The Reactivity of Keratin."

An innovation in the afternoon was a joint meeting with representatives of the International Council of Tanners. Three of their members addressed the conference.

H. A. Densham—"The Economic Situation of the Industry and the Need for Developing Cooperation between Research Workers and Publicity Authorities."

Prof. Dr. W. Grassman—"The Scientific Basis of the Physical Merits of Leather."

J. Beaufils—"The Work of Leather Propaganda Experts in the Advocacy of the Merits of Leather."

Tuesday, September 17

The whole day was given over to a symposium on Leather Manufacture with a panel of experts to conduct the discussion.

Each subject was introduced by a selected member of the panel of experts as follows:

Soaking	Dr. A. Larsson
Liming	Dr. I. Vizovisek
Bating	H. Comte
Chrome Tanning	E. B. Thorstensen
Vegetable Tannage	G. Kamp
Fatliquoring	Dr. F. H. Kroch

Thursday, September 19

Two sessions were held.

The following papers were read:

Morning

(M. Paniker de Pelach presided)

"Collagen Reactivity with Metals"—Dr. R. Borasky

"Limits of Reliability of the Physical Tests of a Sole Leather"—Prof. Dr. Enrico Simoncini

"Note on the Composition and Analysis of Semi-Chrome Leather"—Prof. D. Ing. V. Kubelka

"The Determination of Sludge in Tanning Solutions"—Dr. Ing. I. Radic

"The Determination of Sediments by Weight in Tanning Extracts"—Prof. Ing. J. A. Sagoschen

"The Relation between Natural and Synthetic Bate Liquors and the Influence of Lime Blast on Bating and Scudding"—Dr. H. G. Green

Afternoon

(Dr. Ing. G. Otto presided)

"Recent South African Developments in Rapid Wattle Sole Leather Tannage"—Dr. S. G. Shuttleworth

"Tannins and Polyphenols of Schinopsis (Quebracho) Spp. Their Genesis and Interrelationship"—H. G. C. King, M.Sc., and T. White, Ph.D.

"Impregnation of Sole Leather with Regard to Improvement of Its Quality"—M. Giroflier and G. Desjours

"The Leather Manufacture in India"—Dr. Sanjoy Sen

"Pigskin and Pig Leather"—Prof. Dr. F. Stather

"Practical One-Bath Chrome Tanning"—E. B. Thorstensen.

Friday, September 20

As on Thursday, two separate sessions were held.

Morning
(G. Kamp presided)

"Some Practical Applications of Colorimetry to the Leather Industry."—J. S. Mudd

"Methods for Determining Water-Soluble Matter in Vegetable-Tanned Leather"—Prof. Dr. Enrico Simoncini

"The Resistance of Leather to Temperatures of 140°C. in Connection with Its Use in the Manufacture of Vulcanized Shoes"—Dr. R. Lasserre

"Determination of Active Power of Chemical Disinfectants by Measuring Electrical Conductivity"—Prof. Dr. Alberto Simoncini

"The Constitution of the Pyrogallol (Tannin) Extracts"—Dr. R. Allegrini and Dr. N. De Pisapia

"Researches on an Indian Vegetable Tanstuff: Babul Bark"—Y. Nayadamma, D. Ramaswamy, A. Nagasiromani, P. V. Rajalakshmi, and Shama Shastry

"A New Tanning Process Using Sulfite Cellulose Extracts"—M. A. T. Hough

Afternoon
(Dr. Ch. Gastellu took the chair)

"A Case History of Quality Control in Chrome Tanning"—F. L. Collins and G. M. Oliensis

"The Influence of Various Masking Salts of the Chrome Tanning Baths on the Swelling of Collagen"—Ing. S. Kalin

"Relation between the Charges of the Leather Fibers and of the Adhesives and Finish Products"—Dr. K. Wolff

"A New Apparatus and Process for Drying Leathers"—Dr. Ing. B. Glozic

After the reading of scientific papers was finished, Dr. H. G. Turley presided over the final meeting of the Conference. While addressing the meeting, he announced the formation of a joint committee of representatives of the Union and the International Council of Tanners.

Names of Union representatives up to date are:

Prof. D. Burton
Prof. W. Grassman
J. Mellebay
Dr. K. N. Pepper
Prof. A. Simoncini

This committee, he stated, was empowered to appoint subcommittees as occasion arose, and it was hoped that the cooperation would be to the common good of both sides of the industry.

Reports were received from the various International Commissions:

Dr. R. Allegrini—Hide Powder
Dr. W. Weber (for M. Queroix)—Tanning Analysis

(In view of the apparent impossibility at present of reaching any form of international agreement, it was decided to abandon this committee.)

Prof. V. Dumoulin—Leather Analysis

(Because of increased pressure of work Prof. V. Dumoulin wished to resign. Prof. A. Engeler had been appointed to take over this committee.)

Dr. R. G. Mitton—Physical Testing
Dr. W. Weber—Colour Fastness and Testing

SOCIAL EVENTS

On Monday evening an official reception was held at the Capitol Palace where a welcome to Rome was given by the Mayor, the Hon. Senator U. Tupini. The Capitol was then open for inspection by the members of the Conference.

A Fashion Parade was held for the ladies on Tuesday evening, and on Wednesday a full day's entertainment was arranged for everybody attending the Conference. This commenced with a short bus tour of the city, followed by a conducted tour of the Vatican Museum and St. Peter's. The Conference was entertained at lunch at Villa d'Este, Tivoli. On returning to Rome a further conducted tour of the Borghese Museum was given. The official banquet of the Congress took place at the Grand Hotel on Thursday evening.

For those members of the Conference wishing to attend, His Holiness the Pope gave an audience at his summer residence, Castel Gandolfo, on the morning of Saturday, September 21.

COUNCIL MEETING MINUTES

October 16, 1957
Tanners' Council Research Laboratory
Cincinnati, Ohio

The meeting was called to order at 9:30 A.M. All officers and Council members were present except Mr. Frank Zeissig. The following people were visitors: Oscar Wederbrand, Clinton Retzsch, Ell Dee Compton, Malcolm Battles, and Carl Telander.

Reading the minutes of the last two Council meetings.—In the minutes of the June 2 meeting it was recommended that on the first page, line 14, the words "report on" should be omitted. The sentence would then read, "President-Elect Maeser reported on the Methods status which he has sent to each Council member." After this change the minutes were approved.

Report of the Technical Committee Coordinator.—Mr. Maeser reported on the activities of the technical committees. He also reported that all changes in the Methods status as approved by the membership and all changes in wording recommended by the various committees have been made in the methods. This will be printed and sent to all active members.

The following changes in committee membership have been made. Dr. Clarke has retired from the Eastern Regional Laboratory and is resigning from the Hide Powder Committee. His resignation was accepted with regret. It was agreed and approved by Council that Mr. Fred Luvisi would succeed Dr. Clarke as the chairman of the ALCA Hide Powder Committee, and that Dr. W. Windus would be chairman of the International Union Commission of Hide Powder. Mr. Carl Telander resigned from the International Union Leather Analysis Commission on Chemical Analysis. The International Commission is being reorganized. The committee was discharged for the present time.

Mr. Maeser advised that the chairmen of all the technical committees have been reminded that their annual reports should be in the hands of the Coordinator by December 1 so that they can be prepared for presentation to Council at the January meeting.

Editor's report.—A letter from Dr. Merrill stated that he had no specific report to make at this time. The Council members had a discussion as to what should be put on the cover of the *Journal*. It is difficult to have a new photograph on the cover every month. Council suggested it would be very appropriate for pictures of the new Council members to be published after the election has occurred. These pictures however would be put inside the *Journal*, not on the outside.

It was approved that the printer be asked to print the volume number and issue on the binding edge of the *Journal*, so that a reader can easily distinguish copies when they are stacked in a group.

Council asked that under "Secretary's Notice" the following notice be published periodically, "If you wish to get your *Journal* promptly, please advise the secretary of any change in your address so that we can correct our records."

Ways and Means Committee report.—Mr. Wederbrand reported that he had solicited several people but was unable to get commitments as to who would serve upon his committee. Council gave him the authority to

select any of the members he finds suitable, then they will be approved by Council. Mr. Wederbrand read the following report on the status of the finances of the organization as of this date. "In reviewing the income accounts, dues and advertising will be within the proposed budget. Subscriptions and SLTC dues look like they will be slightly above the proposed budget. The sale of reprints, Methods, and back issues of the *Journal* will fall below the expected amount of the budget. In general, the income should be equal or slightly above the proposed amount. In reviewing the expenses, we find that most expenses are within the allotted amounts with the exception of printing. The printing cost is approximately $1,500.00 over the amount budgeted. However, $800.00 of this is the index for 1956. In the future the index bill will be received in late January of each year and should not vary to any extent; so it will be included as a current expense each year. This leaves the printing expense $700.00 over for nine months."

Convention Committee report.—Mr. Retzsch reported that the Convention Committee would be the same as it was last year and that all members have agreed to serve. The committee is as follows:

R. Stubbings, *Vice Chairman*
J. Stellmach—*Publicity*
Mrs. H. Bernard—*Women's Activities*
H. Bernard—*Hotel and Transportation*
J. Casnocha—*Entertainment*
F. Klimpl—*Entertainment*
M. Lindsay—*Golf*

The matter of registration was considered. It was agreed that the registration fee for 1958 is to be $8.00 for members and $15.00 for nonmembers. As before, there will be no charge for women attending and the usual courtesy charge for bona fide students. This change was made by a motion of Mr. Lord, seconded by Mr. Wilson, and unanimously carried.

Mr. Retzsch reported about the hotels at Atlantic City. On a motion by Mr. Charles Martin, seconded by Mr. Miller, it was unanimously agreed to accept the dates June 11 to 14, 1961, at the Chalfonte-Haddon Hall Hotel in Atlantic City.

Mr. David Wilson, chairman of the committee appointed to study the matter of the symposium at the annual meeting, made the following report:

> Committee organization be as it may, in every case the real burden of responsibility has fallen on one person's shoulders. So let's face it, why let the organizational work be diluted to the point where it bogs down? As you will see, this thought is involved in our recommendation concerning the definition of authority.
>
> Regarding the subject, we believe that there is yet a vast area to be covered in the field of chrome tanning. Also, we have some thoughts on the details of organization and format.

Generally, our recommendation to the Council is as follows:

Definition of authority:

1. One person shall be selected to act as Chairman of the Leathermaking Discussion. There shall be no definite identification with Production Club, section of industry, etc. He should simply be the best man for the job.

2. This Chairman shall be under the direct supervision of the Convention Chairman, although it is not intended that the latter shall have any direct work connected with the Discussion or its organization aspects. His only responsibility is to follow up and insure that the Discussion Chairman is doing his job properly.

3. The Discussion Chairman shall immediately upon his appointment select his own Secretary (if he feels he needs one) and panel from within the industry (4, 5, or 6 members). This panel should represent a cross section from the standpoint of type of leather (calf, kid, sole, upholstery, side, sheep, for example). They shall not be identified by Production Club, although it should be recommended to the Discussion Chairman that he (or his Secretary) request aid in selection from Production Clubs if he feels he can use such help.

4. The Secretary's responsibilities should include correspondence handling during the organizational period, clearing house for manuscripts submitted, etc. The Secretary's duties might be as extensive as the Chairman may wish. If the Chairman intends to delegate broad duties to his Secretary, he may well make his selection such that they may be in close geographical proximity.

Scope of 1958 *Discussion*:

1. The Subject shall be Chrome Tanning and may include the Preparation of Liquors according to the Chairman's decision.

2. The session shall be planned to occupy the entire day's program, both morning and afternoon of the fourth day.

Outline of suggestion for Discussion Chairman:

1. Select your Secretary and panel immediately.

2. Ask panel members to submit *written* manuscripts to you early (chrome tanning from their own viewpoints). These should not be lectures, but should be provocative thoughts — a panelist's first remarks should be designed to stimulate immediate discussion.

3. Handle format of your program in any way you see fit. One successful method has been to ask each member to speak for about ten minutes on some phase — this can be either consecutive or spaced through the day.

4. Panel members *must* be free to enter discussion at any time.

5. You must present the impression of spontaneity. *It does not come automatically*! It must be stimulated by you and your panel. Work with them; prepare plenty of provocative subjects to use when audience participation slows down.

6. Strive to keep discussion headed in one direction. Don't let audience or panel change the subject if you feel there is more along the same lines yet to be explored.

7. When program is over, immediately begin editing. The most successful method has been to first obtain a single copy from the stenotypist (through Dr. O'Flaherty). Have as many copies made as there were participants. Send them out asking for edition of each participant's remarks along with a deadline for its return. It helps to indicate for each person the sections which he is to edit. As they are returned, transcribe the editions to another master copy which will finally represent the complete edition to be submitted to the publisher.

The committee consisted of C. David Wilson, Chairman, with E. D. Lord and Charles Martin. Upon a motion by Mr. Lord, seconded by Mr. Martin, the report, as submitted by Mr. Wilson on behalf of his committee, was accepted.

After much discussion of the matter a list of possible candidates to become chairman of the Leathermaking Discussion was prepared. From the list of potential candidates Dr. Reuben Henrich, of B. D. Eisendrath Tanning Company, was selected. He has agreed to accept this responsibility on the basis of the recommendations made in the report.

Awards Committee.—President Thorstensen presented the following list as candidates for the Awards Committee, and they have agreed to serve: Mr. Ralph Ewe, Chairman, with Mr. L. Meyer and Mr. B. A. Schiller. The above committee, upon motion by Mr. Miller, seconded by Mr. Lord, was unanimously approved by Council.

Employment bureau.—The matter of establishing an employment bureau at the annual meeting was considered by Council, and upon motion made by Mr. Lord, seconded by Mr. Miller, the matter was dropped.

Nominating Committee.—The Nominating Committee, headed by Dr. R. M. Lollar, reported that their work is under way and they hope to complete it in proper time.

New member.—The application of Mr. Simioni to be transferred from associate to active membership was approved.

Member resignation.—The resignation of Mr. Louis Pine was accepted.

Next meeting of Council.—The next meeting of Council is to be held on Friday, January 10, in Milwaukee at the Plankinton House.

Meeting of the International Union of Leather Chemists Association.—An informal review of the activities at the International Union of Leather Chemists Association was made by those members of Council who had attended this meeting.

Meeting adjourned.—Upon motion made the meeting adjourned at 2:00 P.M.

Respectfully submitted,

FRED O'FLAHERTY, *Secretary*

IRA D. CLARKE RETIRES

After working for the Department of Agriculture for 40 years, first with the Leather and Paper Laboratory of the Bureau of Chemistry in Washington, and then with the Eastern Utilization Research Laboratory in Philadelphia, I. D. Clarke has retired from active work. The Clarkes are spending the winter in Crystal Beach, Florida, and expect to return to Pennsylvania for the summer.

I. D. Clarke has been a member of this association since 1920. He broke into print in our journal in 1921 as coauthor of two committee reports, one with the late F. P. Veitch and the other with Ralph W. Frey. These were the first of no less than 34 papers and reports bearing his name, the most recent of which was published in January, 1957. These papers by no means constitute the sum of his contributions to the *Journal*. As early as December, 1920, there appeared an abstract with the now familiar initials, I.D.C.—the first of many hundreds, if not thousands. For at least thirty years Clarke has abstracted the German journal *Collegium* and its postwar successor *Das Leder*, both for our journal and for *Chemical Abstracts*, thus acquainting our readers with many of the most important contributions to leather science. It was with great satisfaction, not unmixed with relief, that your editor received Mr. Clarke's assurance that he is *not* retiring from abstracting. Speaking for all his many friends in ALCA, we wish "I.D.C." many happy years of well-earned leisure. H.B.M.

CHANGES OF ADDRESS

Murrel A. Brown, 2719 Jefferson Street, Midland, Michigan
Thomas H. Harris, 318 Glenfield Drive, Pittsburgh 35, Pennsylvania
Harold R. Miller, E. I. du Pont de Nemours Company, Box 386, Wilmington, Delaware
Francis O. Schmitt, 72 Byron Road, Weston, Massachusetts
Walter A. Wachholtz, Arthur C. Trask Company, 327 So. LaSalle Street, Chicago 4, Illinois
Wallace Windus, 1437 Bryant Lane, Meadowbrook, Pennsylvania

RESIGNATION

Louis Pine, 712A Broad Avenue, Ridgefield, New Jersey

ABSTRACTS

Southwest Africa as a Source of Hides and Skins. U. Braun. *Das Leder*, **8**, 147–54 (1957).—A description is given of the geographical features and climate of southwest Africa and of the hides and skins of wild and domesticated animals found there. The skins are damaged by insects and butcher cuts and are poorly cured as a rule. They are not sorted to meet the tanners' needs, so that they have not been imported into Germany but go to the U.S.A., Italy, and France. A new process for improving the hides is being developed. They are unhaired, then pretanned with Basyntan P, after which they can be accurately sorted. The tanner can either remove the Basyntan P by thorough washing or let it remain as a pretan. I.D.C.

New Electronmicroscopic Investigations on Collagen. K. Kühn. *Das Leder*, **8**, 25–33 (1957).—A review with 44 references and 21 figures. Kühn, Hofmann, and Grassmann have reported (*Z. Naturforschg.* **11b**, 581 [1956]) that silver grains deposited by the periodate-silver urotropine reaction do not correspond with the dark bands of unsilvered fibers but that deposition depends more on thickness and density of the fiber. Most of the silver is in the outer areas of the fiber, but some is inside, and deposition is independent of whether the silver grains are distributed regularly or irregularly. I.D.C.

Identification of Anthocyanidins, Leuco-anthocyanins and 2:3-Dihydroflavonols in Plant Tissues. David G. Roux. *Nature*, **179**, 305–6 (1957).—Chromatographic characteristics of delphinidin, cyanidin, pelargonidin, robinetinidin, fisetinidin, 3:7:4′-trihydroxyflavylium chloride, and 3:7:8:3′:4′-pentahydroxyflavylium chloride are given. R.M.L.

d-Gallocatechin from the Bark of *Casuarina Equisetifolla Linn.* David G. Roux. *Nature*, **179**, 158–59 (1957).—"Casuarin", isolated in 0.04% yield from the bark of *C. equisetifolla*, has been separated into two components by filter-paper chromatography. Casuarin is probably a mixture of d-gallocatechin (5′-hydroxycatechin) and d-catechin. R.M.L.

Identification of Amino Aldehyde (Aminoplasts) Finishes on Textiles. I. John H. Howard. **II.** Braham Norwick and Erwin Bierig. *Am. Dyestuff Rep.*, **46**, 313–15 (1957).—Rapid tests for identifying aminoplasts on fabrics are presented. Characteristic color tests and a paper chromatography procedure are described which permit identification of the different aminoplasts. R.M.L.

The Tear Strength of Fabrics. Richard Steele. *Am. Dyestuff Rep.*, **46**, 329–35 (1957).—The trapezoid, Elmendorf, and tongue-tear tests are critically examined. The tear strength of a fabric is determined by the tensile strength of its load-bearing elements and the way the tearing load is distributed over the bearing elements. The load distribution for the three tests is examined, and the effect of different types of finishing agents is considered. Long-chain alkyl quarternary salts, acting as surface lubricants, increase tear strength when it is measured by a test emphasizing the response of the fabric to distorting forces,

such as the tongue test. Aminoplast precondensates, which are reacted within the individual fibers, reduce the tensile strength of fabrics, and the tear strength is reduced proportionately in all three tests. Surface resins may either increase or decrease the tear strength, depending on the comparative properties of the resin and the fabric structure and on the tear test that is used. R.M.L.

The Gravimetric Estimation of Medulla in Wool. D. A. Ross and J. B. Speakman. *Textile Research J.*, **27,** 345–51 (1957).—The amount of medulla in wool is determined from the weight of the residue left after specimens of known dried weight have been treated with a 1.6% solution of peracetic acid for 48 hr. at 25°C., followed by a 1.0 *N* solution of ammonia for 24 hr. at 25°C. A correction to the results must be applied for the amount of residue given by non-medullated wool, and samples previously dried at elevated temperatures give high residue weights. R.M.L.

Molecular Organization in Keratins. I. Introductory Survey. II. The Density of Native Keratins. R. D. B. Fraser and T. P. MacRae. *Textile Research J.*, **27,** 379–90 (1957).—Methods for the determination of the crystallinity of keratins include water sorption measurement, deuterium exchange experiments, infrared and X-ray diffraction methods, and determination of density. An apparatus for rapid density determination is described in which small keratin specimens may be dried and anhydrous solvent distilled onto the dry specimens, the density being determined by finding the temperature at which the specimen fibers neither float nor sink. In addition to this temperature it is necessary to know the nature of the temperature-density relationship for the immersion solvent. Proper use of the apparatus permits determination of the density of small samples with a precision of 0.001. The relationship between the density values thus obtained and theoretical deductions based on assumptions of different molecular models is discussed for different keratins. R.M.L.

Influence of Ionizing Radiations of Wool Fiber Properties. R. A. O'Connell and M. K. Walden. *Textile Research J.*, **27,** 516–18 (1957).—Important single fiber properties of wools irradiated by X rays, gamma rays, and cathode irradiation have been investigated. No evidence of the introduction of new cross links into wool was found. Radiation doses up to 5 million REP can be given without appreciable damage, but progressive damage is noted at high radiation levels. Ultraviolet irradiation causes immediate, rapid degradation of wool fiber properties independent of the mixture content of the wool. R.M.L.

Research at Springfield College May Standardize Combat Footwear. Anon. *Leather and Shoes*, **133,** No. 14, 8 (1957).—During the past two years Dr. P. V. Karpovich, research professor of physiology at Springfield College, working at the request of the Quartermaster Corps, conducted extensive tests on Army boots made from the conventional Munsen and the so-called "functional" last. The new functional last being tested contains one major change from the conventional Munsen last. A wedge is inserted in the medial side, similar to arch supports in some civilian shoes. This is called the Fort Knox 5 last. The experiment with the boots will continue for an additional six months, at the end of which time Dr. Karpovich hopes to have determined (1) which of the

boots tested is most comfortable for the foot soldier, (2) which recommended changes should be adopted and which discarded, and (3) what type of laboratory test can be used for quick approval of boots. The Fort Knox 4 last for low quarter shoes has been adopted by all branches of the service. J.J.

Research Report from Madras. Anon. *The Leather Mfr.*, **74,** No. 7, 17 (1957).—This report from the Central Leather Research Institute lists the studies undertaken and the achievements accomplished during 1955–56. The studies undertaken were curing; development of enzymes; investigating vegetable materials as tanning agents; fundamental research on vegetable tan particles; developing new fatliquors, syntans, synthetic leather oils, finishes, shoe polishes and stains; and new processes covering a variety of leathers. The achievements listed were 65 processes on a variety of leather; 51 processes covering finishes, syntans, fatliquors, synthetic leather oils, shoe polishes and stains; 4 processes for obtaining enzymes; 11 processes for manufacturing leather board; 2 methods utilizing splits for production of fancy leather; and the development of standard specifications for East India tanned leather, chamois leather, chrome lace, and russet leather. J.J.

Quick Tannages. W. Petrie. *Leather Trades Review*, **124,** No. 3714, (1957).—The author discusses soundness of tannage versus speed of tanning "setting" effects, the advance in knowledge about quick tannage, and the need for more thorough knowledge of the effects of different proportions of various tans, non-tans, and acids to quicken tannages without sacrificing soundness. J.J.

Sheepskin Processing. F. O'Flaherty and J. J. Tancous. *Leather and Shoes*, **133,** No. 22, 16 (1957).—The authors believe that the quality of sheepskin leather has a direct relationship to its handling and processing before tanning. They discuss the flaying, collecting of skins, washing of fresh and salted skins, sulfide painting and the liming and sulfiding in removing the wool, washing and bating after the removal of the wool, pickling of the skins, and the need for a preservative in the pickling operation as steps in the processing of sheepskin. J.J.

Task Group Makes 50 Suggestions for Research on Hides, Leather. J. Huttlinger. *Leather and Shoes*, **133,** No. 17, 43 (1957).—The task group on Hides, Skins, and Animal By-Products submitted to the White House Commission on Increased Industrial Use of Agricultural Products a program calling for $3,000,000 for research. The suggested research was for (1) structures of hides, proteins, and animal by-products and basic chemistry and molecular analyses; (2) research for hide and skin and animal by-products; (3) improvement of curing methods; (4) new uses for leather; (5) parasitic diseases affecting hides and skins; (6) mechanical damages to hides; (7) effects of antibiotics, gamma rays, and radiation on hides and animal by-products; (8) feeding of cattle and sheep as affecting hides and skins. J.J.

American Syntans Today. P. S. Chen. *Leather Mfr.*, **74,** No. 7, 37 (1957).—The author lists the syntans manufactured in this country and the information the manufacturers provide regarding their products. J.J.

Foundation Reports Research Findings on Salt as Curing Agent. Anon. *Leather Mfr.*, **74**, No. 4, 33 (1957).—Dr. E. P. Marbach and Dr. F. L. De Beukelaer of the American Meat Institute Foundation, working with salt- and brine-cured hides and comparing with fresh hides as control, report that they found (1) an increase in the lime-soluble protein upon curing and (2) the removal of the nonleathermaking proteins by salt as partially unsubstantiated. A plausible reason is given for the increase in lime-soluble protein. As salt is not an ideal preserving agent nor the ideal dehydrating agent, the article concludes that there may be a simpler, more effective, and economical way to preserve hides than with salt. J.J.

Investigations on the Behavior of Leather Auxiliary Agents with the Aid of Radioactive-marked Substances. I. The Mode of Action of Wetting, Dispersing, and Emulsifying Agents. R. Heyden, J. Plapper, and K. Sauerwein. *Das Leder*, **7**, 100–7 (1956).—The favorable action of wetting or dispersing agents in lime, pickle, or tan liquors is well known. The question of whether a residue of these agents remains in the leather and affects the water take-up of the leather has been answered by Herfeld who reported no effect. The residue is too small to determine by chemical methods, but radioactive-marked wetting agents can be used. Radioactive sulfur, atomic weight 35, a beta-ray emitter with a half life of 87 days was used; extremely small amounts were needed. Measurements could be made on sections 50–70 microns thick obtained by splitting the leather into over 40 horizontal sections. Because of nonuniformity of the hide, measurements on adjacent pieces differed by as much as 20%. The radioactive balance during tannery operations was in error by up to 20% because of loss of liquor, hair, flesh, tissue, etc. Active dodecyl sulfate (DS) was prepared by sulfating pure dodecyl alcohol with chlorosulfonic acid having a radioactivity of 10 mc, and removing the hydrochloric acid gas with a stream of dry air. This acid ester was dissolved in petroleum ether, neutralized with alcoholic sodium hydroxide, then, after removing water and petroleum ether by distilling at reduced pressure, it was recrystallized from boiling ethanol. Alkylbenzenesulfonate was prepared by sulfonating alkylbenzene ("Korenyl") in 3 volumes of carbon tetrachloride, with S-mc-marked chlorosulfonic acid at 30°–35°C. After distilling off carbon tetrachloride, the product was neutralized; after distilling off water, it was dissolved in alcohol and filtered to remove inorganic salts; then it was extracted with petroleum ether to remove unaltered hydrocarbon. The latter compound was used in the soak liquors in a concentration of 0.3 g. per l. Dodecylsulfate (DS) was used as follows: 0.5% on the hide weight (0.5 g/l) in the soak liquor; 0.2% (0.5 g/l) in the limes; and 0.25% (2.5 g/l) in the pickle. Measurements are briefly described. The equipment must be standardized and corrections made for countersensitivity, geometry of the system, decay of the activity, etc. The beta radiation is very weak, so a Geiger counter with a very thin (0.005 mm.) window must be used. The activity in liquors was measured by first destroying organic matter, then precipitating the sulfur as barium sulfate. If the amount of sulfur was low, enough sulfate (nonradioactive) was added so the limit of self-absorption (of radiation) was exceeded in the sample for measurement. The radioactivity of hides and leather was measured directly in the sections and also after ashing and precipitating sulfur as barium sulfate. When DS was added to the soak water, and not at any later stage, the soaked hide contained 18%, the limed hide 7%, and the finished leather 3.1% of that added. The leather contained 0.017% of DS. This

amount of wetting agent (50 g. per cubic meter) had no bad effect on the leather properties but produced better leather with fine grain. Most of the DS was concentrated in the grain layer at about the level of the hair roots, with a small amount near the flesh surface. If added to the limes, the limed hide contained 6.1% and the leather 3.7% of the DS added, with 0.013% in the finished leather. Distribution was about the same as that when DS was added to the soaks. If added to the pickle, 36% of that added was found in the finished leather, and the DS content of the leather was 0.2%. Tannage in a vegetable liquor containing 2% DS resulted in absorption of 20% of that present and a DS content of the leather of 0.49%. Tannages were also made with Lorikal D, a special fatty alcohol sulfonate (a product of Böhme Fettchemie, Düsseldorf) used for chamois-type leather. With 3% DS, take-up was 69%, with 6.35% in the leather. With 1.5% DS, take-up was 83%, with 3.4% in the leather. Distribution was as before, except for greater amounts throughout the leather. In general, increasing the amount of wetting or dispersing agent used increases the amount found in the leather. If used in one stage of tanning, less should be used in following stages, because some is carried over from stage to stage. Much more is retained in the skin in acid than in alkaline solutions. Water-absorption properties of the leather will not be increased more than is desirable unless too much wetting agent is used. Small amounts of the low-molecular, anionic-dispersing agents added to vegetable tan liquors increase the rate of penetration and uniformity of distribution, protect the grain of the leather, and increase tensile strength.

I.D.C.

PATENTS

Waterproofing Leather. Brit. Pat. 773,347. Midland Silicones, Ltd. Appl. June 7, 1955.—Leather, whether tanned, tawed or otherwise cured, either finished or unfinished, or from various types of animals, such as horsehide, pigskin, kid or cowhide, is rendered water-repellent by impregnating it with a solvent solution (e.g. Stoddard solvent) of a composition consisting essentially of a mixture of (1) 15 to 50 per cent (by weight) of $Zn(OR)_4$, where R is an aliphatic hydrocarbon radical containing less than 13 carbon atoms or a hydroxylated aliphatic hydrocarbon radical containing less than 13 carbon atoms and less than 4 hydroxyl radicals, or an aliphatic hydrocarbon-soluble partial hydrolysate thereof; (2) 5 to 70 per cent of a copolymer resin composed essentially of trimethylsiloxane and SiO_2 units, the units being in such proportion that the ratio of methyl radicals to Si atoms is from 1 : 1 to 2.5 : 1; and (3) 15 to 80 per cent a polysiloxane of the formula:

$$R^1_nSiO_{\frac{4-n}{2}}$$

where each R^1 is an alkyl or alkenyl radical containing less than 6 carbon atoms or a monocyclic aryl radical and n has an average value of 2 to 2.9.

Bactericidal Paper; Proofing against Biological Attack. Brit. Pat. 770,966. American Sugar Refining Co. Appl. Nov. 23, 1954.—Fabrics, paper and leather may be impregnated with fungicidal and bactericidal heavy metal-

quaternary ammonium coupled compounds of hydrophilic colloids by treating them in a bath containing the co-ordination compounds formed from the reaction of the hydrated heavy metal oxides and the hydrophilic colloids and then treating the resulting product in a second bath of quaternary ammonium compound solution to insolubilize the desired impregnant. Leather is stated to be prevented from deterioration by this treatment.

Coated Fabrics. Brit. Pat. 771,080. Kellogg Co., M. W. Appl. July 24, 1954. —Materials such as paper, leather, glass, wood, iron, copper, aluminum, ceramic sheets and asbestos, may be coated with a resinous polymer of trifluorochloroethylene applied from a dispersion comprising the polymer and a plasticizer dispersed in a liquid medium comprising water and a wetting agent which comprises a water-soluble organic oxygenated compound, the mixture having been formed by directly admixing a powdered polymer of trifluorochloroethylene and the plasticizer in finely-divided form with the liquid medium. The polymer may contain up to 15 per cent of another monomer such as vinyl chloride, tetrafluoroethylene, perfluoropropene or acrylonitrile. The plasticizer may be a liquid or waxy polymer of trifluorochloroethylene, or a chlorinated diphenyl or diphenyl methane. The organic oxygenated compound may be an alcohol having not more than 8 carbon atoms per molecule, such as methanol, ethanol, propanol, butanol, pentanol, hexanol, octanol, methoxy ethanol, ethoxy ethanol, butoxy ethanol and ethoxy, ethoxy ethanol, a ketone having not more than 6 carbon atoms per molecule, such as acetone, methyl ethyl ketone, and diethyl ketone or a polyethylene oxide of the non-ionic type wetting agents having not more than 30 carbon atoms per molecule, such as a polyethylene oxide substituted at one terminus with a thioalkyl group or with an alkyl phenoxy. Fillers and pigments such as calcium silicate, calcium carbonate, carbon black, titanium dioxide, phthalocyanines and chrome green may be added to the dispersion.

Artificial Leather. Brit. Pat. 775,597. Deutsche Gold - und Silber - Scheiden - stalt Vorm-Roessler. Appl. Jan. 7, 1955.—In the production of artificial leather comprising a woven, knitted, or netted fabric coated with plasticized polyvinyl chloride by a transfer process from a temporary support, e.g. of paper or metal foil, the temporary support is precoated with a lacquer which is more weakly adherent to the temporary support than to plasticized polyvinyl chloride and which is capable of preventing migration of the plasticizer, so as to produce an artificial leather which is dry to the touch and is not readily soiled. One or more layers of paste may be applied. The lacquer may comprise a polyacrylic acid or polymethacrylic acid ester, preferably polymethyl methacrylate. The support may be provided with embossing before or after coating with the lacquer. A pattern may be printed on the lacquered support. The adhesion betweeen the barrier lacquer and the support may be weakened by a silicone lacquer coating.

Fat Liquoring Emulsions. Brit. Pat. 773,825. Nopco Chemical Co. Appl. Feb. 10, 1955.—An emulsifiable fat-liquoring composition for leather comprises a mixture of (i) a raw oil, which may be either a mineral oil, a fatty oil, or a mixture of such oils; (ii) an anionic surface active agent comprising a "sulphonated" (sulphated) fatty oil, either alone or mixed with a "sulphonated" aliphatic monocarboxylic acid; (iii) a non-ionic surface active agent consisting of an ester of a polyethylene glycol, of average molecular weight 200–300, with

an aliphatic monocarboxylic acid with a carbon chain length of 8 to 18, either alone or mixed with a similar ester in which the polyethylene glycol has an average molecular weight of 300—400 and the acid carbon chain length is 12 to 22; (iv) a cationic surface active agent comprising an alkylated, or cyclized (to a glyoxalidine) and alkylated, derivative of an amino amide of the general formula $R_1CO\ (NHCH_2CH_2)_nNHR_2$, wherein R_1 is aliphatic chain of at least 7 carbon atoms, R_2 is hydrogen or an alkylol group with 1 to 3 carbon atoms, and n is 2, 3 or 4 when R_2 is hydrogen, and 1, 2, or 3 otherwise; and (v) water. Raw oils, which may be used separately or in admixture, include moellon, 28°Bé paraffin oil, white and yellow mineral oils, rice bran oil, neatsfoot oil, sperm oil, fleshing grease, castor oil, herring oil, and cod oil, and are included in amounts of 30—70 per cent, but preferably 45—55 per cent, of the composition. The anionic surface-active "sulphonated" oils may be "sulphonated" sperm, neatsfoot, cod, herring, or whale oils, or "sulphonated" tallow, and may be mixed with, for example, "sulphonated" oleic acid or coconut oil fatty acids. The "sulphonated" oils are present in amounts of 25—50 per cent, preferably 30—40 per cent, of the final mixture. Preferably the SO_3 content of these oils is in the range 4—10 per cent, and the water content may be up to 25 per cent. The polyethylene glycol esters may be either the mono- or the diesters; several examples are given, but a preferred mixture is one of polyethylene glycol (200) monolaurate and polyethylene glycol (400) monolaurate. In such mixtures the polyethylene glycol (200) ester should comprise not less than 40 per cent of the total of the non-ionic esters, and preferably comprises 50—60 per cent. The alkylated cationic amino-amide derivative is made by the condensation of a polyalkylene polyamine, an alkalylene alkylol polyamine or a polyalkylene alkylol polyamine, which may contain 2—4 amino groups, with an aliphatic monocarboxylic acid with a carbon chain length greater than 8 and preferably 8—24, followed by alkylation of the product; several examples are given. These cationic compounds are present in 2—10 per cent, preferably 2—4 per cent, concentration of the final mixture. A preferred example of such a compound is that derived from oleic acid and *N*-aminoethyl ethanolamine. The components of the composition may be mixed in any order, suitably at a temperature slightly above room temperature, but if a cloudiness occurs, this may be dissipated by the incorporation in the final mixture of 0.5—2 per cent, preferably 0.5—1 per cent, of 30°Bé sodium hydroxide solution. Numerous examples are given, some of which describe the treatment of leather with compositions according to the invention.

Tanning Leather. Brit. Pat. 777,474. St. Lawrence Corp., Ltd. Appl. July 5, 1954.—Hides are tanned by impregnating with an aqueous solution containing a water-soluble aldehyde, a water-soluble dibasic acid amide or a water-soluble condensation product of said aldehyde and said amide, together with a water-soluble lignin material at a *p*H effective to maintain the active agents in solution and to cause them to penetrate the stock and thereafter adjusting the *p*H to precipitate the active agents in insoluble form within and on the hide to tan it. As aldehydes the following may be used: formaldehyde, furfural, acetaldehyde, glyoxal and crotonaldehyde or substances yielding aldehydes such as paraformaldehyde trioxymethylene and hexamethylene-tetramine. Formaldehyde is preferred. Amides specified are urea, thiourea, sulphurylamide, oxamide, malonic acid amide, succinic acid amide, biuret and di-thio-biuret as well as urea yielding substances such as amides not of themselves sufficiently water-

soluble but which may be solubilized by a strong acid. The water-soluble lignin material employed is obtained by evaporation of waste liquors from sulphite or sulphate pulping processes, or from the insoluble residue in cellulose saponification processes which has been treated with caustic soda and precipitated by acidifying the solution. The *p*H of the impregnation and fixation steps will depend on the lignin material employed; for example, for waste sulphite liquor the soaking step must be above 3.5 whilst for lignins derived from the kraft or alkaline sulphite process the *p*H should be above 8.5. For the fixation step the *p*H should be above 8.5. For the fixation step the *p*H when employing lignins from sulphite liquor should be from 3.5 down to 2.5 or for alkali lignins, particularly kraft liquor, a *p*H down to 5.5 suffices. The *p*H adjustment in the soaking step may be effected by buffers such as sodium acetate, formate or phosphate or ammonium chloride, whilst the lowering of the *p*H in the fixation step is accomplished by acidifying preferably with hydrochloric acid but optionally with acetic acid, alums, sodium bisulphite, sodium bisulphate, aluminium sulphate, ammonium sulphate, ammonium chloride, ammonium nitrate, sodium hydrosulphite, zinc chloride, aluminium chloride, lactic acid, oxalic acid, phosphoric acid, sulphuric acid or nitric acid. The amount of active tanning ingredients may range from 5 to 100 per cent by weight of solids based on the hides treated. Suitable proportions for the active ingredients are:—water-soluble lignin derivatives 40 to 60 per cent, amide 20 to 40 per cent and aldehyde 17 to 30 per cent. According to a typical example pickled side stock was soaked overnight in a *p*H adjusting solution containing thiosulphate, sodium chloride, bicarbonate and formaldehyde and then drummed in a tanning solution containing sodium chloride, thiosulphate, urea, sulphite waste liquor solids, formaldehyde and water. After drumming for eighteen hours the solution was acidified with hydrochloric acid down to a *p*H of 1.7.

Tanning Leather. Brit. Pat. 777,699. Boeme Fettchemie Ges. Appl. Jan. 27, 1953.—Hides and skins are tanned by consecutively applying thereto a nitrogen containing artificial resin pre-condensate and a water-soluble surface-active compound containing an aliphatic, cycloaliphatic or araliphatic radical of at least 6 carbon atoms, and during the treatment or subsequent thereto converting the water-soluble artificial resin pre-condensate into an insoluble form. The water-soluble surface-active compound may be anion-active, cation-active or electro-neutral. The anion-active compounds are fatty alcohol sulphonates, water-soluble salts of alkyl or alkyl-aryl sulphonic acids or of sulphonated oils or fats, or water-soluble salts of fatty acids, resin acids and wax acids, or water-soluble condensation products of proteins or their degradation products with fatty acid halides, or with sulphonic acid halides which contain radicals of at least 6 carbon atoms or with high molecular weight halogen fatty acid esters or amides. The cation-active compounds are quaternary ammonium compounds and the corresponding phosphonium or sulphonium compounds which contain at least one high molecular weight lipophilic radical, for example trimethyl octadecyl ammonium choride, dodecyl pyridinium bisulphate and dimethyl cyclo hexyl octadecyl ammonium chloride. Electro-neutral compounds are polyalkylene oxide addition products, such as ethylene oxide addition products, of high molecular weight carboxylic acids, amines, mercaptans or of high molecular weight aliphatic or aliphatic-aromatic sulphonic acids or sulphonamides, or the corresponding water-soluble condensation products with polyvalent alcohols such as ethylene glycol, glycerol, pentaerythritol, and sorbitol. The water-soluble

nitrogen containing artificial resin precondensates are those obtained from urea, thiourea, cyanamide, methylene diurea, guanidine, alkyl guanidines, dicyandiamide, dicyandiamidine, and melamine by condensation with aldehydes particularly formaldehyde or acetaldehyde. The resinous tanning agent is generally employed in an amount between 2 and 10 per cent by weight of the unhaired hides whilst the water-soluble surface-active compounds may constitute 2 to 5 per cent. The conversion of the water-soluble resin pre-condensate into insoluble form may be effected by alkaline or acid reagents or by heat. There may be employed in addition to, or as partial replacement for, the water-soluble surface-active compounds, substances such as animal or vegetable fatty acids, for example olein, animal or vegetable fats or oils such as train oil, tall oil and resin oil, mineral oils or fats, fatty acids or sulphonic acid chlorides such as alkyl benzene sulphonic acid chlorides, or other substances containing fatty radicals with reactive halogen atoms such as high molecular weight halogen fatty acid esters or amides. According to examples: (1) sheepskins were defatted, delimed and drenched and then treated at 18° to 20° C. for 2 hours with 4 per cent of a water-soluble melamineformaldehyde pre-condensate and 80 per cent of water. The tanning liquor was then replaced by 5 per cent of an alkyl sodium sulphate mixture and 20 per cent water, and after one-and-a-half hours the leathers showed a *p*H of 6.2, the resin pre-condensate having been converted to insoluble form to complete the tanning. (2) Dehaired goatskins were treated with 3 to 4 per cent of a water-soluble dicyandiamide-formaldehyde condensate and 80 to 100 per cent of water at 10° to 20°C., the leather having a final *p*H of 6 to 6.8, whereby the conversion of the resin pre-condensate into insoluble form commenced. The liquor was then replaced by 3 to 4 per cent of a water-soluble ethylene oxide addition product to an alkyl benzene sulphonamide mixture and 20 per cent water and allowed to stand for an hour, by which time the leather had a *p*H of about 6 and the conversion of the resin pre-condensate into insoluble form was completed. (3) Dehaired calfskins were treated with 4 per cent of a water-soluble urea formaldehyde pre-condensate and thereafter with a solution of 6 to 12 per cent of sodium alkyl benzene sulphonate and 20 per cent of water at normal temperature, the *p*H finally being adjusted to 4.5 to 5 by the addition of an organic acid such as formic acid which converted the resin pre-condensate into insoluble form. (4) Dehaired lambskins were treated with 2 to 3 per cent of a water-soluble melamine-formaldehyde pre-condensate at 18° to 20° C., the leather having a final *p*H of 6.9. The tanning liquor was then replaced by 2 per cent of an alkyl sulphate mixture neutralized by triethanolamine and after treatment the leather had a *p*H of 5.8 to 6.4. Potash, alum and common salt were then added to lower the *p*H to 4 to 4.4 whereby the resin pre-condensate was converted to insoluble form. (5) Sheeps pelts after heating were treated with a pickle containing cooking salt, sulphuric acid and formic acid and thereafter treated at 20° C. with an aqueous solution of oleyl sodium sulphate. Subsequently they were treated with 4 per cent of a condensation product of dicyandiamide and formaldehyde which was converted into the insoluble form since the *p*H of the pelts was already in the acid range.

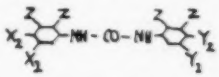
Heat Resistant Leather. Brit. Pat. 777,062. Stokes & Co. (Tanners), Ltd. Appl. June 30, 1955.—A heat-resistant material is composed of a leather base impregnated with asbestos. The impregnated base may subsequently be coated with an asbestos paste. The asbestos as a water paste may be mechanically worked into the leather by drumming. The material can be made into gloves,

aprons, coats, armlets, leggings or headgear to provide protection against dry heat.

Coated Leather. Brit. Pat. 777,293. Farbenfabriken Bayer Akt.-Ges. Appl. June 2, 1955.—Leather is dressed by treatment with an aqueous emulsion of a copolymer containing at least 45 per cent of a butadiene and a smaller quantity of 1,1-dichloro-ethene. In examples, aqueous emulsions of a copolymer of butadiene, 1,1-dichloro-ethene and acrylonitrile (± styrene) are mixed with aqueous leather body colours, lustring agents, plasticisers and water, applied to leather, e.g. buffed cowhide, and dried. Two or more coatings may be applied and hardened by spraying on 10 per cent formaldehyde solution between each coating. Specification 678,614 is referred to.

Filling and Retanning Leather. Brit. Pat. 777,827. Sellet, L. Appl. Dec. 1, 1953.—Leather is treated with a modified aminoplast resin (prepared by reacting an aminoplast resin having at least one reactive methylol group with a water-soluble amine base, the amine base being used in an amount sufficient to eliminate all reactive methylol groups from the aminoplast resin) and an anion-active high molecular weight sulphur compound in an acidic environment, whereby condensation takes place in situ. The leather may be first impregnated with the resin and then the sulpho compound or with the sulpho compound and then the resin or they may both be applied simultaneously. When both the compounds have been absorbed, an acidic compound such as sulphuric acid, citric acid, lactic acid, diglycollic acid, an acidic salt such as aluminium sulphate, aluminium chloride or sodium bisulphate is added to give a *p*H of e.g. 3 to 4. Specified aminoplast resins are the condensation products of formaldehyde with urea, thiourea, guanidine, melamine, dicyandiamide, and acetylene urea, which amines, with the exception of thiourea, are also specified amine bases. Specified sulpho compounds are lignin sulphonate or the sodium or magnesium salt thereof, vegetable tannings, e.g. wattle or quebracho extract solubilized by sodium bisulphite or the sodium, potassium or ammonium salts thereof, and synthetic exchange tannins having at least one sulpho radical or the sodium, potassium or ammonium salts thereof. Many examples of the exchange tannings, which include compounds formed by joining two aromatic residues by a methylene, sulphone, propane or sulphonimide bridge, are given, the sodium salt of disulphodihydroxy-diphenyl propane being preferred. In examples, chrome tanned calf skin is retanned by the method of the invention.

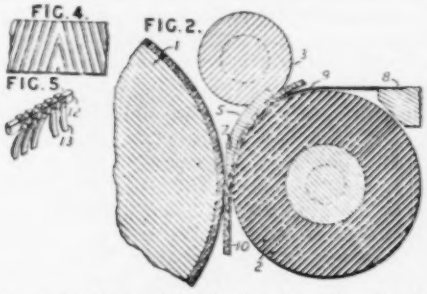
Proofing against Insects. Brit. Pat. 774,802. Geigy, Akt.-Ges., J. R. Appl. June 16, 1954.—Keratin fibres, e.g. wool fibres, are protected against insect attack by treatment with diphenyl urea compounds of the general formula



wherein one X represents a trifluoromethyl group, the other X represents hydrogen or halogen, one Y represents halogen, the trifluoromethyl or the nitro group and the other Y represents hydrogen, halogen or an alkoxy group and Z represents hydrogen or halogen (*see* Group IV (b)). Carriers mentioned include dialkyl ketones, chlorobenzenes, nitrobenzene, etheylene glycol monoalkyl

ethers and pyridine bases. The finely ground active ingredients or organic solvent solutions thereof may be employed as aqueous dispersions. Dispersing agents such as condensation products formed from formaldehyde and naphthalene sulphonic acid or alkylene polyglycol ethers of phenols containing higher aliphatic or alicyclic hydrocarbon ring substituents are specified. In Example (9) wool is boiled in a dispersion comprising N,N¹ - bis - (3 - trifluoromethyl - 4-chlorophenyl)-urea, glycol monomethyl ether, sulphonated castor oil, sulphuric acid and water.

Soft Leather Buffing Machines. Brit. Pat. 777,045. Jenkins, E. L. B., Simon, M. A. B., and Kane, E. A. B. Appl. Nov. 4, 1953.—In a leather buffing machine of the type having a high-speed rotary work cylinder and a work advancing means (normally a feed roll, which is preferably resilient), the pinch roll that usually co-operates with the feed roll or equivalent, to feed the leather and control its passage past the work cylinder, is replaced by a static platen arranged to provide a gap for the introduction of leather to be fed between the lower surface of the platen and the feed roll, the platen



extending to a line near the bite of the feed and work rolls. As shown in Fig. 2, a leather buffing machine is made up of a buffing roll 1, a feed roll 2 having a resilient and deformable outer surface, and a feedtable 8 which has an extension 9 following the curvature of roll 2. The static platen of the invention 5, consists of a blade terminating in a chamfered trailing edge 7 between the rolls 1 and 2, supported on a rod 3. The leather 10, fed between the lower surface of the static platen and the table extension 9 is forced against the feed roll by the platen 5 which is preferably curved on a radius slightly greater than that of roll 2 and centred at a point along the plane of the axes of rolls 1 and 2 to the right of roll 2, thereby forming a tapering throat between the platen 5 and the roll 2. The leather leaving the trailing edge 7 is thereby flexed as shown. The underside of the platen may be provided with diverging grooves as shown in Fig. 4 to spread the hide out on the feed roll or alternatively the platen 5 may be made up of a series of spring teeth 13 (Fig. 5) suitably divergent as shown and supported on and secured to a rod 12. As a further alternative the static platen may consist of a vertical plate mounted above the point of contact of the work and feed roll or equivalent, the extension 9 of the table 8 in this case being extended around the feed roll 2 for almost 90 degrees.

Tanning Agents. Brit. Bat. 773,508. Boehme Fettchemie Ges., Appl. June 22, 1954.—Tanning solutions containing fatty substances and a high proportion

of chromium or aluminium salts and common salt are prepared with the aid of a dispersing agent consisting of a condensation product of a polyalkylene oxide wax, having a molecular weight above 1000, a phosphoric acid or anhydride thereof or a chloride of phosphorus, and an aliphatic, alicyclic or aliphatic-aromatic compound which contains at least 6 carbon atoms per molecule and contains an exchangeable hydrogen atom linked to oxygen, sulphur or nitrogen. Specified condensate components are (1) polyoxyalkylene waxes: polyoxyethylene wax of molecular weight 5000—10,000, and polyoxypropylene wax; (2) phosphorus containing components: orthophosphoric acid, phosphorus pentoxide, trichloride and oxychloride; (3) exchangeable hydrogen-containing component: fatty, naphthene, cyclohexyl, alkylated cyclohexyl, and resin alcohols; alkyl phenols and alkyl naphthols with C_3—C_{18} alkyl residues; the corresponding amines, mercaptans, carboxylic acids, amides and sulphonamides. In examples: (1) an emulsifier prepared from polyoxyalkylene wax, phosphorus oxychloride and dodecyl alcohol is mixed with spindle oil and sulphonated olein, and the paste mixed with a chrome tanning solution and employed for brush tanning of fur skins; (3) a dispersant prepared from polyoxyalkylene wax, phosphorus oxychloride and dodecylbenzenesulphamide is dissolved in water, and commercial chlorparaffins containing 30—60 per cent by weight of chlorine, and decalin are stirred in. Chromic oxide is then added and the composition used as in (1).

Retanning Leather. Brit. Pat. 776,956. Koppers Co., Inc. Appl. May 5, 1955. —Mineral-tanned leather is wetted with water in excess of that which it will absorb, drained, mixed with solid resorcinol, the mixture contacted with formaldehyde or a formaldehyde-liberating agent and the *p*H of the liquid established and maintained at 6–7.5 until the formaldehyde and resorcinol are exhausted. 2–5 per cent of resorcinol based on the wrung-out levelled weight of the leather is used and 1.5–3.0 mol. formaldehyde &c. is used per mol. of resorcinol. The leather may have been tanned with chromium, alum, zirconium, titanium, iron, copper or zinc; as formaldehyde-liberating agent, paraformaldehyde, hexamethylene tetramine, ethylene diamine formaldehyde or hydantoin formaldehyde may be used; magnesium oxide, sodium bicarbonate, potassium carbonate, sodium carbonate, calcium carbonate, magnesium carbonate, calcium oxide and /or calcium hydroxide may be used to maintain the *p*H. In a preferred embodiment, paraformaldehyde and an alkali, especially sodium carbonate, are used together in a weight ratio of 2:1. Both mixing with resorcinol and contacting with formaldehyde may be carried out by drumming, and temperatures of 100–140°C. are used in the examples. It is stated that the hair on hair-on hides treated by this process are more silky and of improved adherence.

Enzymatic Dehairing. Brit. Pat. 776,323. Rohm & Haas Ges. Appl. June 21, 1955.—Green or soaked skins are dehaired by applying a pulverulent protease composition, preferably to the flesh side, and after permitting slackening to take place, removing the hair. The skin is preferably first soaked in the presence of a bacterial protease and if desired of a carbohydrase; the skin is then sprinkled with the protease composition and after standing or tumbling in a drum for a sufficient time, e.g. at 18–20°C., it is dehaired immediately or after covering with water for a period. Subsequently the skin should be further slackened with alkaline swelling agents such as caustic alkalis or with lime and sodium sulphide as swell-limer. Specified materials are: *proteases* derived from mould fungi (e.g. Aspergillus parasiticus and A. flavus), or bacteria (e.g.

Bacillus subtilis) or from the pancreas, preferably with the addition of a carbohydrase (which may be derived with the protease, e.g. from B. subtilis, or otherwise, e.g. from A. orycae): *activating agents*—reducing sulphur compounds, nitrates, nitrites: *preservatives*—sodium phenylphenolate: *additional materials*—ammonium sulphate, sodium bisulphite, sulphite. It is stated that the invention is applicable successfully, in contradistinction to the prior art, to calf skins and fresh or dried and salted sheep skins. Specification 154,103, [*Class* 76], and German Specification 263,873 and 386,017 are referred to.

Oiling and Waterproofing Leather. Brit. Pat. 776,375. Boehme Fettchemie Ges. Appl. Nov. 8, 1954.—Esters and amides of unsaturated fatty acids or esters of unsaturated fatty alcohols and mono- or poly-basic carboxylic acids, in which the ethylenic double bonds are wholly or partly epoxidized are incorporated into leather or fur skins by the usual methods of applying oils, such as oiling off, fulling or hot stuffing, e.g. in the form of aqueous emulsions. The applied compound contains at least 12 carbon atoms; 2 to 10 per cent (based on the weight of leather) of the unsaturated fatty acid derivatives, or 2 to 20 per cent of the unsaturated fatty alcohol derivatives are generally required. The materials may be bound to the leather &c. more firmly by heating to a temperature of 60° to 100°C. after the usual drying. Specified materials which may be epoxidized and used are: (a) natural oils, fats or waxes, i.e. unsaturated fatty acids such as olive oil, linseed oil, soya bean oil, neat's foot oil and sperm oil esterified with glycerol, or the alkyl, cycloalkyl, alkylcycloalkyl, or alkylaryl esters, e.g. hexyl, octyl, dodecyl, oleyl, glycol, polyglycol, polyglyceryl, cyclohexyl, naphthenyl, abietyl, and alkylphenyl (C_3–C_{18}) esters of said fatty acids; (b) amides of unsaturated fatty acids, e.g. the amide or amide mixture from oleic acid or linseed, soya bean or train oil fatty acids, oleic acid mono- and di-ethanolamide, linseed oil fatty acid cyclohexylamide and oleic acid piperidide; (c) esters of unsaturated alcohols obtained by reduction of animal or vegetable unsaturated fatty acids or by splitting natural wax esters (e.g. oleyl alcohol) with mono- or poly-carboxylic acids such as maleic, citric, adipic, diadipic (a tetracarboxylic acid comprising 2 molecules of adipic acid) and phthalic acid. In addition to the epoxidized material, other oiling agents (e.g. neat's foot oil, marine animal oils, and mineral oils), and anionic, cationic or electrically neutral emulsifiers (e.g. alkyl sulphates, alkyl sulphonates, alkylbenzene sulphonates, sulphonated oils, fats or train oil, quaternary ammonium compounds or ethylene oxide addition products) may be used. In the examples, the following mixtures are employed: (1) epoxidized train or sperm oil/C_{14}–C_{16} fatty alcohols/aqueous alkyl sulphates/stearic acid-ethylene oxide addition product; (2) epoxidized soya bean oil/Turkey red oil; (3) epoxidized olive oil or epoxidized oleyl butyrate/aqueous alkyl sulphates/cationic emulsifier prepared by reaction of the dodecyl ester of chloracetic acid with hexamethylenetetramine/polyethylene glycol esterified with stearic acid (the epoxidized olive oil could be replaced with epoxidized neat's foot oil); (4) the emulsion specified in (1) together with titanium dioxide (after tanning, trimming, after-tanning and neutralization with sodium thiosulphate); (5) epoxidized dioleyl ester of phthalic acid/aqueous alkyl sulphates/polyethylene glycol esterified with stearic acid; (6) epoxidized phthalic acid ester of unsaturated alcohols produced by reduction of linseed oil fatty acid/aqueous ethylene oxide-oleyl alcohol addition product/polyethylene glycol stearic acid addition product. The anionic emulsified oils of (1) could be used in combina-

tion (e.g. subsequently with an interposed acidification to *p*H 4.5 to 4.7) with the cationic-emulsified oil of (3), especially after combined or synthetic tanning. The procedure of (4) above, is stated to achieve improved water-repelling properties.

Waterproofing Leather. Brit. Pat. 777,078. General Electric Co. Appl. Feb. 1, 1955.—The water-repellency of leather is improved by treating it with an aqueous emulsion containing the polymerizable fluid intercondensed product of hydrolysis of a mixture composed essentially of 50 to 75 per cent by weight, of dimethyldichlorosilane, 1 to 10 per cent of trimethylchlorosilane, 10 to 35 per cent of methyltrichlorosilane, and up to 10 per cent of a methylchlorodisilane or mixture of methylchlorodisilanes, and a curing agent for such product, comprising a metal salt of an acid, the metal ion being present to the extent of at least 2 per cent of the weight of the hydrolysis product, and the weight of the hydrolysis product being from 0.2 to 20 per cent of that of the aqueous emulsion, and curing the said hydrolysis product. The methylchlorodisilane or mixture of methylchlorodisilanes may comprise dimethyltetrachlorodisilane, methylpentachlorodisilane and trimethyltrichlorodisilane. A suitable mixture of methylchlorosilanes may be obtained by passing methyl chloride over silicon in the presence of copper at elevated temperatures, as described in Specification 575,667, [*Group* IV]. Small amounts of other compounds are produced which may be removed before the mixture is hydrolysed. The salt may be a water-soluble salt of a metal of Group IV of the Periodic Table, e.g. a salt of titanium, zirconium, tin or lead or a complex of such a salt; water-insoluble salts which are soluble in the methylpolysiloxane hydrolysis product or are dispersible therewith, e.g. zinc or tin octoates or naphthenates may also be employed. Emulsifying agents such as morpholine oleate, ammonium-oleate, sulphonated amide condensation products of fatty acids with organic amines, sulphonated aromatics and mixed alkylaryl sulphonates, sulphonated esters and fatty acid amide condensates may be used in making the dispersions. Stabilizers such as 2-methylpentanediol-2,5 may be added to the diluted emulsions, as used for treatment, to prevent premature breaking thereof, and improve penetration. Plasticizers, e.g. paraffin oil, paraffin wax, neatsfoot oil, tricresyl phosphate and dimethylphthalate, bonding agents, resins, e.g. polystyrene, polyvinyl chloride, copolymers of vinyl chloride and vinyl acetate and polymethylmethacrylate, and drying oils such as chinawood oil, oiticica oil and linseed oil may be incorporated in the emulsion. Treatment may be by drumming the wetted leather, which may have been pre-treated by drumming it with dilute aqueous ammonium hydroxide, followed by neutralization and rinsing, with the methylpolysiloxane emulsion, and then curing by drying, with or without heat. The leather may subsequently be treated with finishing agents, e.g. alkyl polyacrylate emulsions in conjunction with neutral or synthetic rubber lattices, the adhesion of which is improved by priming its surface with organic silicates or partially hydrolysed organic silicates as described in Specification 711,374, [*Group* III]. Specification 745,154, [*Group* IV (a)], and U.S.A. Specifications 2,635,059 and 2,635,060 are referred to.

Tanning. Brit. Pat. 772,440. Boehme Fettchemie Ges. Appl. Sept. 11, 1953. —Hides and skins are tanned using as tanning agents condensation products derived from dicyandiamide, a carbonyl compound, particularly formaldehyde, and a sulphite (*see* Group IV (a)). The products may be used as sole tannins

or their use combined with formaldehyde, chromium or aluminium salts or mineral, vegetable or other synthetic tannins or resin or fatty tannins. The tannins may be converted on the hide to the insoluble form by treatment with acids or salts or by heat treatment. In examples: (5) drenched hides are treated with 80–100 per cent water and 10 per cent of condensation product for 1–3 hours and then acidified to *p*H 4.5 with formic acid. The hides are subsequently beaten, neutralized and liquored. For soft leathers the acidification is omitted. (6) Goatskins are treated with 80–100 per cent water and 3–4 per cent condensation product, beaten, fulled in an oleyl sodium sulphate solution and finally treated with 2 per cent potash alum in water, dried and stretched. (7) Drenched calf-skins are tanned with the condensation product, acidified, further tanned by the addition of chromium oxide, and worked up as usual. (8) Delivered and drenched hides are pretanned with the condensation product with the subsequent addition of, acidified and after-treated with vegetable and synthetic tanning agents. (9) Similar to (8) but using soft cowhide and different vegetable tannins. (10) Sole leather is obtained by pre-tanning with the condensate and after-tanning with a strong synthetic tannin/vegetable tannin brew for 3–5 weeks. (11) Chrome-tanned calf-skins or neat hides after neutralization and fatting are treated with 1–3 per cent of condensation product for 2 hours, dried next day and further treated as usual for velour leathers. (12) Skins are treated with 0.5–1.5 per cent of condensation product and 0.5 per cent alkyl sodium sulphate for 3 hours to 1½ days (according to thickness of hide) in a rotating vessel. The rotation is stopped and the skins allowed to remain overnight in the vessel after which they are fulled up and adjusted to *p*H 4.2 to 4.6, the vessel being rotated. The skins are stacked for 1–2 days, rinsed for 10 minutes and after-tanned with a mixture of vegetable and synthetic tannins, preferably with the addition of alkyl sodium sulphate. The leather is stored for one day, pared, rinsed and fat liquored. For white leathers the vegetable/synthetic tannin mixture is replaced by a suitable synthetic tannin. For softer leathers the amount of alkyl sodium sulphate is increased.

Leather Tanning Emulsions. Brit. Pat. 772,454. Boehme Fettchemie Ges. Appl. June 23, 1954.—Dispersing agents produced by condensing a polycarboxylic acid with a polyalkylene oxide wax and simultaneously or subsequently with a compound containing a reactive OH, NH_2, SH, $CONH_2$ or SO_2NH_2 group (see Group IV (a)) are used for the production of saliferous dispersion of fatty substances for the production of tanning oils which also contain common salt and chromium or aluminium salts. In Example 3 a paste is prepared from spindle oil, olein sulphate and an emulsifier prepared from polyethylene oxide wax, citric acid and octadecyl alcohol. This paste is mixed with a solution containing sodium chloride and basic chrome tanning salt to produce an emulsion suitable for stroke tanning. Example 4 is similar using an emulsifier from polyethylene oxide wax, diadipic acid and an alkyl-sulphamide with C_{12}—C_{18} alkyl residue. In Example 6 an emulsifier from polyethylene oxide wax, octadecyl alcohol and an oleic acid–maleic anhydride adduct is used to emulsify neutralized sulphonated fish oil. This emulsion is mixed with sodium chloride, basic chrome tanning salt and fat to produce an emulsion suitable for tanning.

Process of Retanning Leather with a Condensation Product of Sulfones of Monohydric Phenols, Non-Aromatic Amines and For-

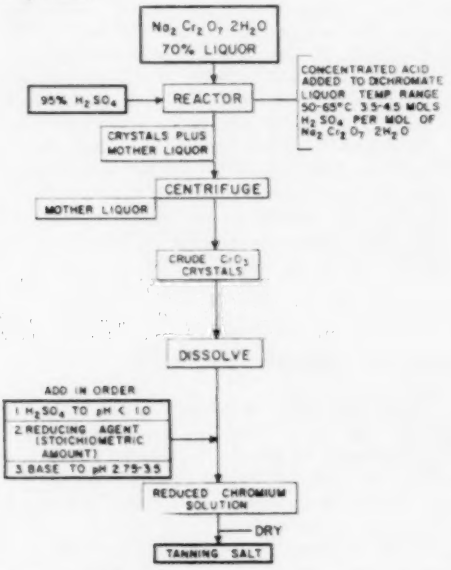
maldehyde. U. S. Pat. 2,809,093. Martin Meister, Leverkusen-Wiesdorf, and Gustav Mauthe, Opladen, Germany, assignors to Farbenfabriken Bayer Aktiengesellschaft, Leverkusen, Germany, a corporation of Germany. Appl. July 7, 1953.—1. Retanning process which comprises retanning a previously tanned leather with a tanning liquor containing up to 25% of a salt of a condensation product obtained from sulfones of monohydric phenols with non-aromatic mono-amines and formaldehyde at temperatures abut 100°C.

Process of Producing White Tanned Leather by Precipitating in Situ Zinc Sulfide and Sulfhydrate Compounds and Product Produced Therefrom. U. S. Pat. 2,809,878. Harlan A. Depew and George R. Waitkins, Kirkwood, Mo., assignors to American Zinc, Lead & Smelting Company, St. Louis, Mo., a corporation of Maine. Appl. May 13, 1954.—1. A process for tanning hides consisting of the essential steps of impregnating the hides with a water soluble sulfide selected from the group consisting of potassium, sodium, barium, calcium, and ammonium sulfides, and then impregnating the hides with a zinc salt selected from the group consisting of zinc chloride and zinc sulfate, there being sufficient quantities of water soluble sulfide and zinc salt employed to precipitate in the hides sufficient amounts of a zinc sulfide selected from the group consisting of zinc sulfide, zinc sulfhydrate, and basic zinc sulfides to tan the hides.

Method of Treating Furs. U. S. Pat. 2,807,557. Clifford R. Carney, Seattle, Wash. Appl. April 16, 1951.—3. The method of treating fur pelts to provide a long-lasting, soft, pliable leather and natural and pleasant appearing hair having a non-oily texture comprising the novel steps of wetting the surfaces of the pelt with an oil in water type of emulsion containing in its disperse phase a hydrocarbon-soluble hydrocarbon polysiloxane oil and a hydrocarbon-soluble hydrocarbon polysiloxane resin and a hydrocarbon wax, and continuing said wetting until the composition has thoroughly penetrated the pores and interstices of the skin, thereafter drying the pelt and agitating the fur hairs.

Leather Pasting. U. S. Pat. 2,805,952. George K. Greminger, Jr., Midland, and Miles A. Weaver, Ithaca, Mich., assignors to The Dow Chemical Company, Midland, Mich., a corporation of Delaware. Appl. August 10, 1954.—1. A liquid adhesive composition, especially adapted for leather pasting, consisting essentially of a water solution of (*a*) from 81 to 93.95 percent, based on the total weight of solute, of a water-soluble cellulose ether having a gel point between 45° and 75°C. and containing from 1.5 to 2 alkyl groups of from 1 to 2 carbon atoms and from 0 to 0.8 hydroxyalkyl groups of from 2 to 3 carbon atoms per $C_6H_{10}O_5$ unit; (*b*) from 5 to 15 percent of a water-soluble plasticizer for the cellulose ether; (*c*) from 1 to 3 percent of casein; and, (*d*) from 0.05 to 1 percent of a water-soluble amine, the concentration of the solute in water being adjusted to provide a solution whose viscosity is appropriate to the intended method of application of the adhesive; the amine being one which gives smooth aqueous solutions of casein with a pH from 7 to 8 when 15 parts by weight of casein is soaked for 30 minutes at room temperature in 80 to 85 parts of water, the resulting mixture is stirred and warmed to 60°C., 5 to 15 percent of the amine is added, based on the weight of casein, and the mixture is held at 60°C. for 30 minutes while stirring.

Method of Preparing a Tanning Composition Comprising Basic Chromic Sulfate. U. S. Pat. 2,805,117. Tom S. Perrin, Painesville, Ohio, assignor to Diamond Alkali Company, Cleveland, Ohio, a corporation of Delaware. Appl. Sept. 8, 1953.



1. The method of preparing a tanning composition comprising basic chromium sulfate, which includes the steps of providing a substantially saturated solution of an alkali metal dichromate, adding to said solution sulfuric acid in an amount of from 3 to 4.5 moles of H_2SO_4 per mol of alkali metal dichromate, said acid having a concentration substantially within the range of 78%–104.5% H_2SO_4 by weight, maintaining the temperature of the mixture of said acid and said solution substantially within the range of 50–65°C. until CrO_3 crystals precipitate, separating said CrO_3 crystals from the mother liquor so as to leave a comparatively small amount of the mother liquor adhering to said crystals, dissolving said crystals and mother liquor in water to form a solution containing chromic acid, adjusting the pH of the chromic acid solution with a strong mineral acid to a value below 1.0, reducing the hexavalent chromium of said solution to trivalent chromium by applying an aqueous solution of a chemical reducing agent, adjusting the pH of said trivalent chromium solution with an aqueous alkaline solution to a point substantially within the range of 2.75–3.5, drying the aforesaid solution and recovering therefrom the resulting composition containing basic chromic sulfate.

Method of Vegetable Tanning Completely Delimed Hides. U. S. Pat. 2,804,367. Raymond L. Moore, East Aurora, and Harland T. Markley and Joseph J. Baker, Buffalo, N. Y. Appl. Oct. 5, 1954.—5. The method of tanning which comprises soaking a depilated and partially delimed hide in an acidic

aqueous solution of pH 5 to 6 and above the iso-electric point of the hide, said solution being initially free of salts, until the pH of the solution has changed and is above the pH range 5 to 6, then constantly adjusting the pH of said solution by adding acid thereto to maintain the pH thereof in the range pH 5 to 6 and above the iso-electric point of the hide until the pH of the solution in contact with the hides remains constant for two hours in the pH range 5 to 6, thereby producing in the hide itself a persistent pH in the range 5 to 6 and above the iso-electric point of the hide, the hide being substantially lime free and then adding tannin to the hide by soaking the hide in a vegetable tanning extract at room temperature and of a concentration of 75 to 85 barkometer at a pH of about 1 to 3 pH units above the iso-electric point of the hide until the tanning extract has penetrated to a predetermined depth in the hide and then neutralizing the alkaline condition of the hide in the absence of excess tanning extract above that required to tan the hide with a buffered acid to lower the pH of the hide below its iso-electric point and until the tanning extract is fixed by the hide to produce leather.

BOOK REVIEW

A Survey of Fellmongering, Calfskin and Hide Production, and Leather Manufacture in New Zealand and Australia. Henry Phillips. British Leather Manufacturers' Research Association, Egham, Surrey, England. 1957. 38 pages. Price: 7 shillings, 6 pence.—The scope of this pamphlet is evident from its title. The author, who was then the Director of the B.L.M.R.A. Laboratory, spent about a month in New Zealand and two in Australia making a thorough study of the subject. The result is a clearly written, concise, and intelligently critical account of the present state of the hide and leather industries in the "down under" Commonwealths. The report includes a summary of research activities in the skin and leather field in the two countries and a section on the production of vegetable tanning materials in Australia.

H.B.M.

ERRATA

In "Tanning with Radioactive Chromium" (*JALCA*, **52**, 476–83, September, 1957) the following corrections should be made:

p. 478, l. 3: for "IR-120-B" read "IR-120-H."

p. 478, l. 29: for "(15)" read "(16)."

p. 479, l. 19: insert "(15)" after "previously reported".

p. 482, l. 12: the second formula should read

$$[CrOx(H_2O)_4]\ [Cr^*Ox_2(H_2O)_2]$$

p. 483, Table III: The first formula should read

$$[Cr(H_2O)_6]\ (ClO_4)_3$$

p. 485, Table V: The fifth formula from the top in column one should read

$$[CrOx(H_2O)_4]\ [CrOx_2(H_2O)_2]$$

p. 487, l. 11: The formula should read

$$[CrOx(H_2O)_4]\ [Cr^*Ox_2(H_2O)_2]$$

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If the leather being tanned is to receive a subsequent application of a water-repellent product fatty in nature, we recommend the use of 2% of Nopcolene R based on the pickled weight of the stock. Start the chrome tanning operation; after 30 to 45 minutes, add the Nopcolene R. Proceed in your usual manner with tanning, neutralizing, retanning and dyeing.

For leathers that are not to receive additional water-repellent fatty material, we suggest using 3 to 4% of Nopcolene R added as above. On certain types of leather, such as calfskin and sheepskin, it is possible to eliminate entirely a separate fatliquoring operation. Where an extremely soft piece of leather is desired, refatliquoring may still be done and the amount of topping oil can be reduced in direct proportion to the amount of Nopcolene R employed.

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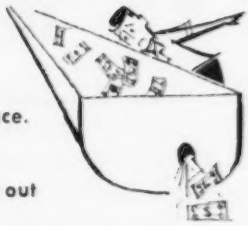

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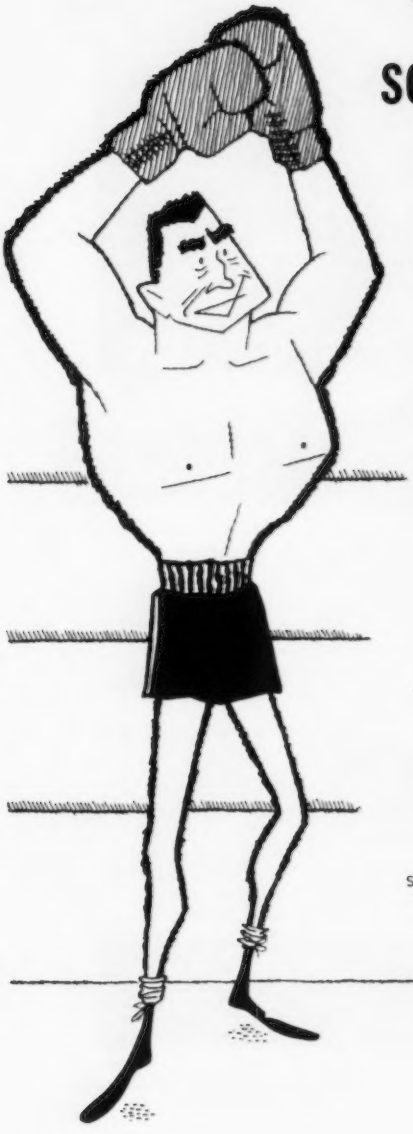

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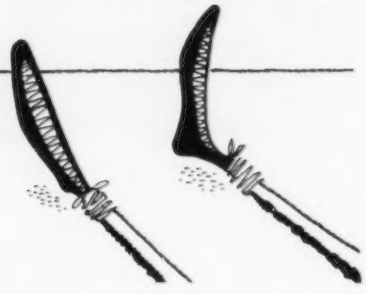

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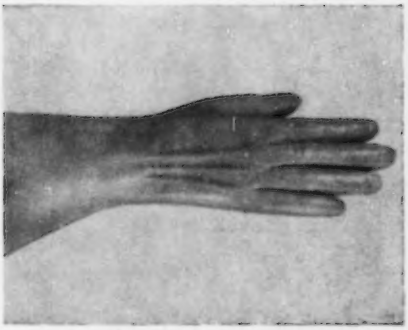
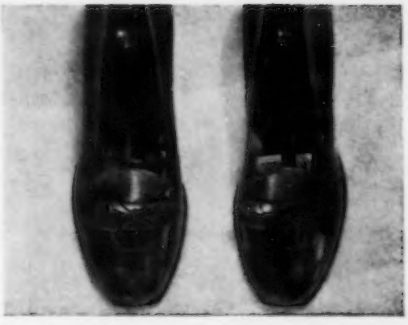
WALLERSTEIN COMPANY, INC. XX
WARNER CO. XXXIII
WHITTEMORE-WRIGHT CO. XXII
WOLF, JACQUES & CO. VII
YOUNG CO., J. S. XVI





for uniformity in Chrome Tanning specify dependable

MUTUAL SODIUM BICHROMATE

When you use Mutual Sodium Bichromate in the preparation of your chromic tanning bath you can be confident that there will be dependable consistency in its traditional high quality. The unvarying high purity of Mutual's product eliminates the possibility of bichromate problems in liquor formulations. This is assured by Mutual's rigid continuous quality control testing during manufacture.

Remember, too, that Mutual technical service, backed by over 100 years of manufacturing experience, is available to you when you need it—from America's *first* producer of chromium chemicals.

For those who want a prepared one-bath chrome tan of assured uniformity, Mutual supplies KOREON in two types—KOREON M at 33-35% basicity and KOREON X at 50-52% basicity.

Mutual Chromium Chemicals

MUTUAL

Sodium Bichromate
Sodium Chromate
Chromic Acid

Potassium Bichromate
Potassium Chromate
Ammonium Bichromate

Koreon (One-Bath Chrome Tan)

MUTUAL CHROMIUM CHEMICALS
SOLVAY PROCESS DIVISION
Allied Chemical & Dye Corporation
61 Broadway, New York 6, N. Y.

Allied Chemical

Please send:

- ☐ Bulletin No. 107—"Preparing Basic Chromic Sulfate Tanding Liquors from Sodium Bichromate"
- ☐ Bulletin No. 108—"Analytical Methods for Bichromate Reduction Control"
- ☐ Booklet No. 54 – "KOREON One-bath Chrome Tan for Leather" L3-5-1

NAME_____

POSITION_____

COMPANY_____

STREET_____

CITY_____ ZONE____ STATE_____

Show-how!

Chemtan is always ready to share with you its years of know-how and show-how in practical tanning and experience in the chemical fundamentals involved.

CHEMTAN R-4 and R-6

Chemtan R-4 and R-6 represent a group of resins which have gained world-wide recognition within a few years. They are high polymers, yet water soluble and will penetrate untanned or tanned hides. Their high filling value and other properties mean making better leather from inferior hides.

There are unlimited possibilities of creating new types of leather or modifying established procedures. Chemtan R-4 and R-6 may be applied on chrome tanned leathers or be used at any other stage and combined with all known tanning agents. One of Chemtan's Tannery and Laboratory Trained Men will be glad to demonstrate these products.

CHEMTAN COMPANY
EXETER, NEW HAMPSHIRE

CHEMTAN COMPANY

EXETER, NEW HAMPSHIRE

All our facilities are devoted exclusively to the tanning industry

American Leather Chemists Assoc. Jnl.

PART II OF NO. 1 IS THE INDEX FOR THE PREVIOUS VOLUME--NO NEED TO BE REPLACED IN THIS VOLUME.